MINERAL SURFACES AND HUMIC SUBSTANCES: PARTITIONING OF HYDROPHOBIC ORGANIC POLLUTANTS

Thesis by

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The antipathy of the paraffin-chain for water is, however, frequently misunderstood. There is no question of actual repulsion between individual water molecules and paraffin chains, nor is there any very strong attraction of paraffin chains for one another. There is, however, a very strong attraction of water molecules for one another in comparison with which the paraffin-paraffin or paraffin-water attractions are very slight.

G.S. Hartley (1936)

Water simply loves itself too much to let some substances get in its way.

J.N. Israelachvili (1985)

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Abstract

The influence of aqueous chemistry on the sorption reactions of three polycyclic aromatic hydrocarbons (PAHs) with Suwannee River humic substances and with an inorganic fused silica surface was examined using fluorescence techniques. By varying the pH, ionic strength and composition of the background electrolyte, the influence of solution chemistry on carbon-normalized partition coefficients and surface area-normalized reaction quotients and adsorption constants was observed. The humic substances examined in this study were present as freely dissolved species and as organic coatings on colloidal-sized aluminum oxide particles.

Binding of the PAHs by dissolved and adsorbed humic material was complete within 3 minutes for all samples; several reactions with dissolved humic substances appeared to be equilibrated within 20 seconds. The association of a PAH compound with Suwannee River humic material appeared to depend on the size of the solute molecule and its ability to fit into hydrophobic cavities in the humic structure. The adsorption of humic and fulvic acid onto alumina decreased their ability to bind perylene. The ability of adsorbed humic substances to bind perylene was dependent on the type of surface complex which was formed between the alumina surface and the humic material. A major effect of solution chemistry was to alter the adsorption mechanisms of the humic substances, which in turn dictated the types of surface complexes formed.

The adsorption of perylene to a nonporous silica surface required 2½ to 4 hours to reach equilibrium. An apparent equilibrium was attained in 60 to 90

minutes for desorption reactions. Quantitative recovery of adsorbed perylene was observed after a 5- to 10-minute methanol extraction. The observed adsorption rates were correlated with the fugacity of perylene and the surface speciation of fused silica. From long-term adsorption data it appears that two different processes are operative in the adsorption of perylene to the fused silica surface. The nature of these processes is not clear, but may relate to the structure of water at the solid-liquid interface.

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Chapter 1

INTRODUCTION

Humans have always built up their own order at the expense of some order in the environment; in recent history, however, they have multiplied destruction of environmental order to build up increasingly intricate structure of cultural and technical civilization (Stumm and Morgan, 1981). Increasing development of civilization has always been a primary driving force for humans, and has been particularly enhanced by man's unmatched ability to exploit natural resources. However, it has become evident in the past few years that industrial and economic growth has not been without environmental cost (Voice and Weber, 1983). The development of cultural and technical civilization has been marked with increasing interference in hydrogeochemical cycles (Stumm et al., 1983). As humans increasingly have disrupted the cycles connecting the land, water and atmosphere, the ratio of pollutant fluxes to natural fluxes has multiplied.

What is pollution? People usually have a limited (typically egocentric) concept of what constitutes pollution. In a very broad sense, however, pollution is the alteration by humans of our surroundings in such a way that they become unfavorable to present ecosystems. Thus, pollution adversely affects not only people, but also causes other environmental catastrophes such as loss of species and diversity. This characterization implies that pollution not only results from addition of contaminants directly into the environment, but also from other direct or indirect consequences of human activity. Over the years the gross pollutional load has increased and its character has changed, especially in industrialized and highly settled regions. While a few decades ago most of our wastes were predominantly catabolic,

they are now more and more composed of discards of modern industrial society (Stumm and Morgan, 1981).

A realization that chemical contamination of the environment is extensive and significant has emerged, largely as a result of increased awareness and improved methods for evaluation. Certain chemicals are now known to exhibit carcinogenic and/or mutagenic properties in small doses, and the accumulation of these compounds in various compartments of the environment is alarming. The properties of certain chemicals which give them their usefulness are often the same properties which contribute to their significance as environmental and public health threats (Voice and Weber, 1983). A recent well-known example involves the general class of compounds called CFCs and their implication in the destruction of the ozone layer.

One group of chemicals currently receiving attention are polycyclic aromatic hydrocarbons (PAHs), probably the most widespread of all chemical environmental contaminants. Because many PAHs are known to be mutagenic, carcinogenic and/or co-carcinogenic, there is justifiable concern regarding their sources and fate in the environment. PAHs are a diverse chemical class and are known to be relatively persistent in the environment. Member compounds have been found widely distributed in atmospheric particulates, freshwater and various sediments, soils, and leachates (Means et al., 1980).

PAHs are ubiquitous products of the burning of carbon-based materials. They occur as a result of combustion involving carbon and hydrogen and are naturally

present in vegetation and fossil fuels. The environmental sources of PAHs include anthropogenic inputs such as energy production and the transportation, storage, and refining of fuels. In addition, natural inputs such as combustion (forest fires), sediment diagenesis, geologic phenomena (volcanos, tar pits, seepage from rock formations) and biological conversion of biogenic precursors have been identified as sources of PAHs in the environment (Means et al., 1980).

This study focused on investigating sorption reactions of hydrophobic organic compounds (HOC) under laboratory conditions selected to model natural water systems. PAH compounds were utilized as surrogates for nonpolar hydrophobic contaminants, but are also important pollutants themselves as discussed above. Hydrophobic compounds, as their name implies, have relatively low solubilities in water and thus tend to accumulate at surfaces and, particularly, with natural organic material in the environment. An understanding of adsorption mechanisms, therefore, is an important key to describing the fate of HOC in the environment because sorption reactions directly affect the mobility, chemical reactivity, bioavailability, and toxicity of hydrophobic compounds.

The objectives of this research were to:

- Gain a molecular-level understanding of the mechanisms by which PAH compounds partition between dissolved humic material and water
- Elucidate the mechanisms by which humic substances adsorb to a hydrous oxide surface

- Investigate the binding of a PAH compound by an organically-coated hydrous oxide surface and determine what effect the nature of the surface coating has on the ability of the PAH probe to associate with the surface
- Gain a better understanding of the mechanisms of adsorption of a PAH compound on a bare mineral surface
- Determine the effects of pH, ionic strength, and the presence of bivalent cations on the four reactions above

Figure 1 is a conceptual diagram of the mechanisms of interaction which were investigated in this research. Because PAH compounds are nonpolar, the adsorption of a PAH probe at a mineral surface is not shown as a specific-site reaction (Reaction 1). In contrast to PAH adsorption, the interaction between a humic substance and a mineral surface is shown as adsorption at a specific site (Reaction 2), based on the current ideas of organic material adsorption. It should be noted, however, that there may be situations in which nonspecific adsorption of organic material occurs. Reaction 3 indicates the binding of a PAH in solution by freely dissolved humic material, while Reaction 4 depicts the binding of a PAH probe by an organically-coated mineral surface.

The influence of solution chemistry on the association of three PAH compounds (anthracene, pyrene, perylene) with dissolved humic material (Reaction 3) is investigated in Chapter 2. Chapter 3 examines the adsorption of humic substances on colloidal-sized particles (Reaction 2) in order to study the

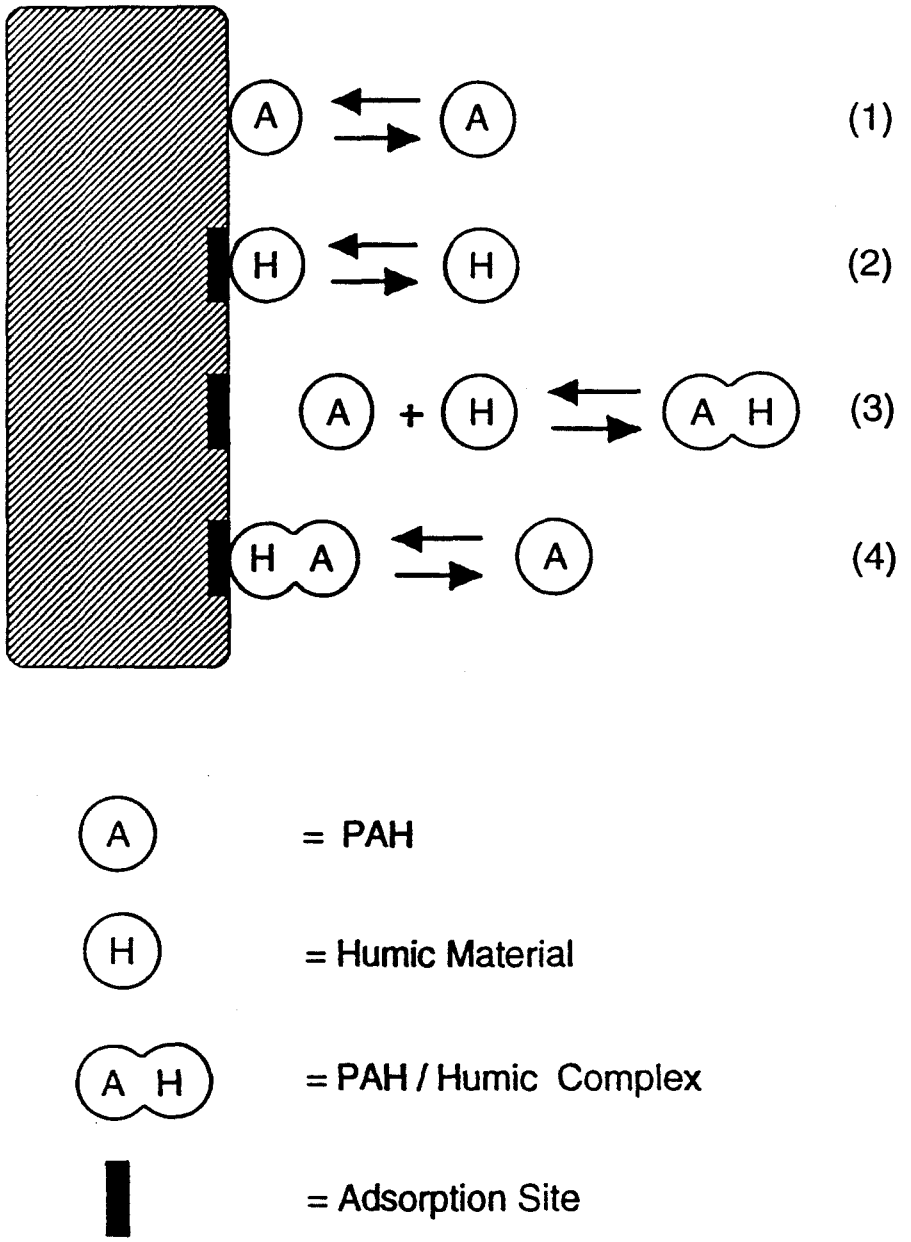

Figure 1. Mechanisms of interaction between a mineral surface, a humic substance and a nonpolar hydrophobic organic pollutant (after Keoleian and Curl, 1989).

effects of aqueous chemistry on the nature and formation of organic coatings on minerals. Results obtained in Chapter 3 are then utilized in Chapter 4, which studies the binding of perylene to organically-coated particles (Reaction 4) and relates the affinity of the coating for perylene to the mechanisms of humic material adsorption. In the absence of organic coatings, adsorption of HOC on bare mineral surfaces may be important (Reaction 1). Chapter 5 investigates the adsorption of perylene on a fused silica surface, and examines the importance of solution chemistry on the interaction. Chapter 6 summarizes the major points from the earlier chapters, and discusses the importance of the different interactions (Reactions 1 to 4 in Figure 1) in the context of natural aquatic systems.

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Chapter 2

THE EFFECTS OF AQUEOUS CHEMISTRY ON THE BINDING OF POLYCYCLIC AROMATIC HYDROCARBONS BY DISSOLVED HUMIC MATERIALS

ABSTRACT

The influence of solution chemistry on the binding of three polycyclic aromatic hydrocarbons (PAHs) by well-characterized humic material (Suwannee River humic and fulvic acid) was examined using fluorescence quenching techniques. The fluorescence of PAH compounds associated with the humic substances was fully quenched as evidenced by quantum yields which approached zero for all complexes. Binding of PAHs by humic material was observed to be complete within 3 minutes for all samples; for many samples, the binding appeared to be equilibrated within 20 seconds. In NaCl solutions, the binding of PAHs by Suwannee River humic material decreased with increases in pH (constant ionic strength) and decreased with increasing ionic strength (fixed pH). The presence of Ca^{2+} had mixed results: at neutral to high pH values it generally increased the binding of PAHs relative to that in NaCl solutions, while at low pH it either decreased the binding or had little effect. From the results of this study, the binding of a PAH compound by Suwannee River humic material appears to depend on the size of the solute molecule and its ability to fit into hydrophobic cavities in the humic molecule.

INTRODUCTION

The partitioning of nonionic hydrophobic organic compounds (HOC) between water and surface soils or sediments has been shown to depend primarily on the hydrophobicity of the compound and the fraction of organic carbon (f_{oc}) in the sorbent (Karickhoff et al., 1979; Means et al., 1980; Chiou et al., 1979, 1981). The mechanism of partitioning results from the "hydrophobic interaction," a combination of relatively small van der Waals bonding forces and a substantial thermodynamic gradient which drives the organic molecules out of aqueous solution (Voice and Weber, 1983). The van der Waals attraction forces between organic molecules are generally dominated by London dispersion forces (induced dipole-induced dipole) with smaller or no contributions from Keesom orientation forces (dipole-dipole) and Debye induction forces (dipole-induced dipole). The thermodynamic driving force is the increase in entropy upon breakdown of the highly-structured coordination shell of water molecules surrounding the hydrophobic solute. The hydrophobic interaction has been discussed in detail by Tanford (1980) and Israelachvili (1985) and the thermodynamics of partitioning have been developed for the octanol-water system and for sediments (Chiou et al., 1982; Karickhoff, 1984; Curtis et al., 1986). Several excellent reviews of the relevance of hydrophobic partitioning in environmental systems have been published (McDowell-Boyer et al., 1986; Weber et al., 1991).

The importance of the organic carbon content of soils suggests that various components of natural organic material in solution may also bind nonionic hydrophobic organic contaminants. Recently, much work has been focused in this

area (Carter and Suffet, 1982; Landrum et al., 1984; Whitehouse, 1985; McCarthy and Jiminez, 1985; Chiou et al., 1986, 1987; Garbini and Lion, 1985, 1986; Gauthier et al., 1986, 1987; Traina et al., 1989; Backhus and Gschwend, 1990). The collective results from these studies suggest that the binding of hydrophobic organic pollutants by dissolved organic material (DOM) depends on the chemical and structural characteristics of the DOM and may depend on the aqueous chemistry of the system.

Partitioning of HOC between DOM and water has been modeled analogously to the dissolution of the compound in an organic solvent; in this case, the DOM is considered to form a "microscopic organic phase." The thermodynamic treatment of partitioning in the octanol-water system has been extended to systems with natural organic material in solution (Chiou et al., 1983; Curtis et al., 1986; Chin and Weber, 1989). Chiou et al. (1983) assumed the major components of humic material were amorphous polymeric substances (macromolecules) and applied the Flory-Huggins theory to estimate solute activity in the humic phase. This was necessary to account for the large negative deviations from Raoult's law, which describes only ideal mixtures. Negative deviations occur when interactions between unlike molecules are markedly stronger than like-pair interactions (Barton, 1983). These interactions cause large entropic effects without the associated enthalpic effects predicted by Regular Solution theory and result because of the large differences in molecular size of solute and polymer.

The objective of this research was to investigate systematically the effects of

pH, ionic strength and the presence of bivalent cations on the binding of organic compounds by DOM. In order to elucidate the effects of aqueous chemistry apart from the effects of the "quality" of natural organic material (e.g., Garbini and Lion, 1986; Chiou et al., 1986; Gauthier et al., 1987), well-characterized humic materials were chosen as models to represent DOM. Aquatic humic substances constitute 40 to 60 percent of the dissolved organic carbon, and are the largest fraction of natural organic matter, in water (Thurman, 1985).

Polycyclic aromatic hydrocarbons (PAHs) were the probes chosen as model organic pollutants. These nonpolar, nonionogenic compounds were selected in order to eliminate or minimize possible adsorption mechanisms other than the effect of hydrophobic interactions in the partitioning reaction. PAHs have been used previously as models for nonionic hydrophobic organic contaminants (e.g., Karickhoff et al., 1979; Landrum et al., 1984; Whitehouse, 1985; McCarthy and Jiminez, 1985; Gauthier et al., 1986, 1987; Traina et al., 1989; Backhus and Gschwend, 1990). PAHs fluoresce in aqueous solution, but the fluorescence is quenched when they are associated with DOM. Thus, the fraction of PAH associated with DOM can be determined without separating the DOM from the aqueous phase.

Several methods have been used previously to study the partitioning of HOC between DOM and water, including dialysis, reverse phase separation and ultrafiltration. These methods rely on the separation of DOM from the aqueous phase to quantify the amount of pollutant associated with the DOM. The inability to completely remove DOM from water has resulted in observations of a "solids effect"

in some studies (Landrum et al., 1984; Gauthier et al., 1986; Carter and Suffet, 1982), in which the measured partition coefficient decreases with increasing concentrations of DOM. In studies which used techniques that did not require a separation (e.g., headspace analysis and fluorescence quenching), a solids effect was not observed (Garbini and Lion, 1985; Gauthier et al., 1986, 1987). Problems with separating DOM from water have been recognized previously as the cause for observed solids effects (Gschwend and Wu, 1985; Morel and Gschwend, 1987; Voice et al., 1983; Voice and Weber, 1985). Therefore, methods capable of measuring the concentrations in situ are ideal because separation difficulties may introduce artifacts in the determination of partition coefficients.

FLUORESCENCE QUENCHING AND ENERGY TRANSFER

The fluorescence quenching technique is based on the observation that PAHs fluoresce in aqueous solution but not when associated with DOM (McCarthy and Jiminez, 1985; Gauthier et al., 1986, 1987; Traina et al., 1989; Backhus and Gschwend, 1990). Fluorescence quenching of PAH compounds by DOM has been hypothesized to be a static quenching process. Gauthier et al. (1986) tried to determine the type of quenching they observed (dynamic versus static) by evaluating the data as a dynamic quenching process, computing the bimolecular quenching rate constant and comparing it to the constant expected for a diffusion-controlled process. Because the computed rate constant (3.2×10^{11} $\underline{M}^{-1}s^{-1}$) was an order of magnitude larger than that expected for a diffusion-controlled process ($\sim 10^{10}$ $\underline{M}^{-1}s^{-1}$), they concluded that the observed fluorescence quenching was a static process.

Traina et al. (1989) made similar calculations for their system and reached the same conclusion. They also attempted to validate a static quenching mechanism by observing the temperature dependence of fluorescence in the presence and absence of DOM. Because dynamic quenching is diffusion-controlled, a dependence on temperature is expected for this fluorescence quenching mechanism. Their data showed that quenching was not sensitive to temperature over the range they examined. Therefore, they concluded that dynamic quenching was not present in their system.

While the previous arguments against dynamic quenching are persuasive, the measurement of fluorescence lifetimes in the presence and absence of a quencher is the best method to ascertain the type of quenching being observed (Lakowicz, 1983). Unfortunately, the fluorescence lifetimes for PAH compounds in the presence of DOM have never been studied.

Because the fluorescence quenching technique does not require separation of the free pollutant from the bound fraction, it is relatively rapid and simple to use. However, the combination of a seemingly simple technique with a lack of understanding of the mechanisms involved have resulted in studies which erroneously claim to have used fluorescence quenching to determine sorption coefficients (Shimizu and Liljestrand, 1991; Liljestrand and Shimizu, 1991). Of the previous studies which utilized fluorescence quenching to examine PAH partitioning, only Backhus and Gschwend (1990) allude to the mechanism by which DOM may statically quench PAH fluorescence.

The mechanisms of energy transfer from an excited organic molecule (donor) to a quenching species (acceptor) have been discussed by Parker (1968), Berlman (1971) and Schulman (1977). A more thorough treatment has been developed by Turro (1978). Therefore, only a brief discussion of the concepts presented by Turro (1978) is warranted.

The radiationless transfer of singlet to singlet energy from a donor to an acceptor can occur via two different mechanisms: an electron exchange interaction and a Coulombic interaction. A major distinction between the two mechanisms is that

in the former interaction electrons are exchanged and therefore collisions are required. Collisions provide the physical contact necessary for overlap of the electron clouds of the donor and acceptor. The Coulombic interaction has no such requirement. Instead the Coulombic interaction represents an "action at a distance" (Turro, 1978). The electrons initially on the excited donor remain with the donor after the energy transfer has occurred. Likewise, the acceptor keeps its respective electrons.

Because the fluorescence quenching of PAH compounds by DOM is not considered to be a diffusional process, the electron exchange (or collisional) interaction is probably not the mechanism of radiationless energy transfer observed. Attention must then be focused on the Coulombic interaction mechanism.

When an organic molecule absorbs light and becomes electronically excited, extensive nuclear geometry changes can occur as well as an enormous dipole moment increase in the excited state relative to the ground state. A molecule which is nonpolar in the ground state may acquire a dipole analogous to the permanent dipoles that participate in some van der Waals (Keesom and/or Debye) interactions. The analogy continues with Turro's description of the Coulombic interaction as a "transmitter-antenna" mechanism in which the electric field near an electronically excited molecule is assumed to behave like a field generated by an oscillating dipole (Turro, 1978). Therefore, the Coulombic interaction is also referred to as the induced dipole or resonance excitation transfer mechanism and can be explained by the Förster theory of Coulombic energy transfer.

Potential acceptor molecules within the electric field around the excited donor molecule may absorb energy from the field and be electronically excited. The transfer of energy from the donor molecule to the acceptor molecule results in the donor's return to its ground electronic state through a radiationless process. The excited acceptor molecule may return to its ground state either by emitting a photon (sensitized fluorescence) or by any of the various radiationless pathways for the deactivation of electronically excited states (Schulman, 1977). Because DOM in general is an inefficient fluorophore, it is likely that the radiationless process of internal conversion is the pathway by which it returns to the ground state.

Förster theory predicts that the Coulombic interaction for radiationless energy transfer will be most favored when (Turro, 1978):

(a) there is a large overlap between the fluorescence emission spectrum of the excited donor molecule and the absorbance spectrum of the acceptor molecule,

(b) the extinction coefficient of the acceptor molecule integrated over the absorption band is large,

(c) there is a small spatial distance between the donor and acceptor molecules (the rate of energy transfer via Coulombic interaction is inversely proportional to the sixth power of the separation distance), and

(d) the radiative rate constant of the excited donor molecule is large.

From the conditions specified above, it should be possible (in principle) to predict whether the fluorescence of a PAH compound associated with DOM will be statically quenched.

It is interesting to note that both the Coulombic interaction mechanism and the electron exchange interaction mechanism predict a direct dependence on the overlap between the fluorescence emission spectrum of the excited donor molecule and the absorbance spectrum of the acceptor molecule (Turro, 1978). This dependence is also seen in a third electronic energy transfer mechanism, the "trivial" or radiative mechanism. This mechanism is more commonly known as being a component of apparent quenching or the "inner-filter effect." In this process, the excited donor molecule emits a photon which is then absorbed by the acceptor molecule. However, the acceptor molecule does not influence the excited donor molecule's ability to emit a photon; rather, it intercepts the emitted photon before the photon reaches the detector (Turro, 1978).

While the radiative mechanism for electronic energy transfer is of no theoretical interest (Parker, 1968), it is an important experimental artifact which must be taken into account. The prevailing wisdom is that the inner-filter effect should be minimized in fluorescence spectroscopy (Lloyd, 1981). However, the mutual dependence of all three quenching processes on the spectral overlap suggests that trying to eliminate the inner-filter effect may result in a decrease in the static (or dynamic) quenching observed in a system.

EXPERIMENTAL

Apparatus. Fluorescence measurements were made on a Shimadzu Model RF-540 Recording Spectrofluorophotometer with a right angle geometric sample chamber configuration. The excitation source was a 150W xenon-arc lamp and excitation and emission wavelengths were obtained with off-plane concave diffraction grating (900 lines/mm) monochromators. The excitation/emission wavelengths used for the PAHs studied are listed in Table I with slits set for the bandwidths shown. Fluorescence measurements of rhodamine 110 were made at the excitation/emission wavelengths of 496/520 nm with slits set for bandwidths of 10 nm on both the excitation and emission monochromators.

Absorbance measurements were made on a Hewlett Packard 8451A Diode Array Spectrophotometer at the appropriate wavelengths to correct for the inner-filter effect. The spectral bandwidth was fixed at 2 nm. The spectrophotometer was equipped with a Hewlett Packard 89055A cell stirring module to allow mixing in the cells.

Fused silica fluorescence cells (Spectrosil, Starna Cells Inc.) with Teflon stoppers were used for both fluorescence and absorbance measurements. Fused silica cells contribute very little background fluorescence relative to quartz cells and are generally recommended for fluorescence work. The cells had a path length of 10 mm.

The pH of all aqueous solutions was measured with a Radiometer Model PHM84 Research pH Meter using a Radiometer GK2401C glass combination electrode. The pH meter was calibrated with NBS buffers.

Table I. Experimental Operating Conditions for Determining PAH Fluorescence.

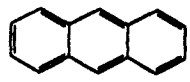
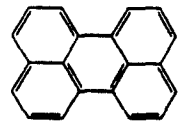
		Anthracene	Pyrene	Perylene
Excitation				
	λ (nm)	250	334	432
	Bandwidth (nm)	5	5	10
Emission				
	λ (nm)	380	390	470
	Bandwidth (nm)	5	5	10

Materials. The PAHs used in this study were anthracene (Aldrich, 98+% pure), pyrene (Aldrich, 99+% pure) and perylene (Aldrich, 99+% pure). Relevant chemical and physical properties of the PAHs are listed in Table II. Rhodamine 110 (Lasergrade) was obtained from Kodak. All were used without further purification. PAH stock solutions were stored in the dark at 4° C in amber borosilicate glass bottles to prevent photodegradation and/or volatilization. Before use, the solutions were allowed to equilibrate (in the dark) at room temperature for at least 24 hours.

Concentrated stock solutions of anthracene (12200 μg/L, 68.5 μM), pyrene (25100 μg/L, 124.1 μM), and rhodamine 110 (2.7 g/L, 7.4 mM) were made up in methanol (Fisher, Spectroanalyzed). Because of its relatively low solubility in methanol, perylene was first dissolved in chloroform (J.T. Baker, Photrex). An aliquot of this solution (120 mg/L, 475.6 μM) was then spiked into methanol to obtain the desired stock concentration. Finally, an aliquot of the concentrated stock of rhodamine 110 was spiked into the perylene stock to obtain the final working stock solution (120 μg/L (475.6 nM) perylene, 30 μg/L (81.8 nM) rhodamine 110 in methanol with 0.1% (v/v) chloroform).

Well-characterized humic materials were obtained from the International Humic Substances Society (IHSS) and used without further purification. Suwannee River standard humic acid and Suwannee River standard fulvic acid were isolated from the Suwannee River which drains the Okefenokee Swamp in southern Georgia. Isolation procedures and characterization of these materials have been reported (Averett et al., 1989). Chemical properties of the humic and fulvic acids are shown

Table II. Chemical and Physical Properties of Polycyclic Aromatic Hydrocarbons (PAHs)

	Anthracene	Pyrene	Perylene
Structure			
Formula	$C_{14}H_{10}$	$C_{16}H_{10}$	$C_{20}H_{12}$
FW (g/mol)	178.23	202.26	252.32
Solid Density (g/cm^3)	1.283	1.271	1.35
mp (°C)[a]	214-217	149-151	277-279
ϕ_F [b]	~0.4	~0.7	~1.0
water solubility distilled[c] ($\mu g/L$)	73	135	0.4
water solubility (nM)	409.6	667.5	1.585
log K_{ow} (M/M)	4.54[d]	5.18[d]	6.50[e]

[a] Supplied by Aldrich.

[b] Quantum yield in aqueous solution [25°C] (Turro, 1978).

[c] MacKay and Shiu, 1977. (measured value)

[d] Karickhoff et al., 1979. (measured value)

[e] Yalkowsky and Valvani, 1979. (calculated by summation of f values)

in Table III and some physical properties are listed in Table IV.

Because the humic materials received are very hygroscopic, they were stored in a desiccator until needed. Concentrated stock solutions were prepared by dissolving weighed amounts of the humic material in deionized, distilled water (D_2H_2O). The solutions were mixed and allowed to stand in the dark for at least 24 hours. The humic stock solutions were filtered through a prewashed 0.2 μm pore polycarbonate Nuclepore filter to remove possible particle contamination and were then stored in amber borosilicate glass bottles similarly to the PAH solutions.

Absorbance spectra and measurements at the wavelength of 250 nm were taken of the humic and fulvic acid stock solutions before and after filtering to check for possible loss and/or fractionation of material. No such effects were observed.

All other reagents were of analytical grade or better and were used without further treatment. All aqueous stock solutions were filtered through 0.2 μm pore polycarbonate Nuclepore filters.

Procedure. (A) General. Aqueous solutions were prepared with distilled, deionized water (D_2H_2O) (Corning Mega-Pure™ System). All experiments were performed at room temperature (23° C) in an open system (i.e., aqueous solutions were equilibrated with the surrounding atmosphere). The open system is a model which approximates the carbonate system of natural waters by equilibrating water with the atmosphere containing $CO_{2\,(g)}$ at a constant partial pressure (Stumm and Morgan, 1981). For waters which are in equilibrium with the atmosphere, the huge reservoir of $CO_{2\,(g)}$ imparts a significant buffering action above pH 7.

Table III. Chemical Properties of IHSS Standard Suwannee River Humic Substances.

Elemental Analysis (%) [a] and Atomic Ratios [b]

(Ash-Free and Moisture-Free Basis)

	C	H	O	N	S	P	Total	Ash	O/C [b]	H/C [b]	C/N [b]
Humic Acid	54.22	4.14	39.00	1.21	0.82	0.01	99.40	3.19	0.54	0.91	52.25
Fulvic Acid	53.75	4.29	40.48	0.68	0.50	0.01	99.71	0.82	0.57	0.95	92.18

[a] Supplied by International Humic Substances Society (IHSS).

[b] Calculated from elemental analysis.

Structural Carbon Distributions [a]

(% of Total Carbon)

	Ketone-C (220-180)	Carboxyl/ Carbonyl-C (180-160)	Aromatic-C (160-105)	Aromatic/ Acetal-C (105-90)	Aliphatic -HCO (90-60)	Aliphatic -CH (60-0)	sp^2 (220-90)	sp^3 (90-0)	Aromaticity f_a [b]
Humic Acid	7	16	42	6	12	17	71	29	0.42
Fulvic Acid	6	19	28	5	15	27	58	42	0.28
group density [c] (g/mL)	1.74	1.878	1.601	1.601	1.620	0.72			

[a] Determined from liquid-state ^{13}C NMR [ppm range shown in parentheses] (Thorn, 1989).

[b] f_a = spectrum area from 160-105 ppm divided by total spectrum area.

[c] Group density contribution to calculated density (Brown and Leenheer, 1989).

Table IV. Physical Properties of IHSS Standard Suwannee River Humic Substances.

	Humic Acid	Fulvic Acid
Radius of Gyration (Å) [a]		
pH 6	11.1	7.2
pH 9	11.4	7.7
M_n (daltons)	1100 [a]	800 [b]
Density (g/mL) [c]	1.508	1.427
v_{app} (mL/g)	0.6631	0.7008
V_p (mL/mole) [d]	730	560

[a] Determined by small-angle X-ray scattering (Aiken et al., 1989).

[b] Determined by vapor-pressure osmometry (Aiken et al., 1989).

[c] Calculated from structural carbon distributions (Table III).

[d] $M_n \div$ Density.

Fluorescence cells were cleaned by repeated soaking and rinsing, first with methanol and then D_2H_2O. Cell cleanliness was monitored with fluorescence and absorbance measurements. All other glassware was cleaned by soaking in either 4 M HNO_3 or 4 M HCl, rinsing repeatedly with D_2H_2O, and drying in an oven at 110° C.

Absorbance spectra were taken to determine the possible wavelengths which could be used for excitation of each PAH. Fluorescence emission spectra were obtained by exciting the PAHs at the wavelength of an absorption band in order to determine wavelengths at which fluorescence could be observed. The fluorescence emission spectrum of a pure substance is independent of the wavelength of excitation (Parker, 1968). Finally, fluorescence excitation spectra were recorded and an appropriate pair of excitation/emission wavelengths were selected for each PAH. Wavelength pairs were chosen to maximize the fluorescence intensity and minimize the background interference (e.g., from quencher fluorescence and/or the Raman scattering of water).

(B) Anthracene and Pyrene. The fluorescence quenching method used was adapted from Gauthier et al. (1986). Sample solutions were prepared by adding an appropriate amount of concentrated salt solution(s) to D_2H_2O in an Erlenmeyer flask and adjusting the pH with 0.1 M HCl and/or 0.1 M NaOH. The samples were stirred until no further pH change was observed, indicating that they had reached equilibrium with the atmosphere. The pH of concentrated humic and fulvic acid solutions was adjusted similarly. pH-adjusted humic and fulvic acid stock solutions

were used within two days to minimize the effects of hydrolysis of the acids (Bowles et al., 1989).

A typical experiment consisted of pipetting 3 mL of a sample of known pH and ionic strength into a fluorescence cell containing a Teflon-covered micro stir bar (7 mm x 2 mm, Spinbar) and recording the absorbance and fluorescence intensity at the appropriate wavelengths. The sample was then spiked with 10 μL of anthracene or pyrene stock solution and stirred for 10 minutes before recording an initial fluorescence intensity and absorbance. Initial PAH concentrations for these solutions were nominally 40.5 μg/L (0.23 μM) for anthracene and 83.4 μg/L (0.41 μM) for pyrene. Preliminary results showed that neither anthracene nor pyrene adsorption to cell walls could be detected over the time period required for a complete experiment, and that solutions were completely mixed in less than one minute.

The PAH solutions were then titrated with humic or fulvic acid (previously equilibrated at the same pH) until a minimum of five aliquots were added. Preliminary kinetic experiments showed that the binding of anthracene and pyrene was always complete within 3 minutes. However, the solutions were stirred for 10 minutes after each addition of humic material to ensure that equilibrium was attained before fluorescence and absorbance measurements were recorded. During the course of an experiment, each PAH solution was kept in the dark while mixing and the shutter of the spectrofluorophotometer was opened only for the actual intensity measurements. Each measurement required approximately 10 seconds. Since duplicate readings were taken for each addition, the total time of exposure to UV

radiation was less than 5 minutes for each experiment. No PAH photodegradation was observed during an experiment.

In order to correct for the background fluorescence contribution of the solution components, a blank sample spiked only with methanol was titrated and analyzed using the same process as for the PAH sample.

(C) Perylene. The fluorescence quenching method used for perylene was adapted from Backhus and Gschwend (1990). Sample solutions were prepared by adding appropriate amounts of concentrated salt solution(s) and varying amounts of humic material stock solutions to D_2H_2O in Erlenmeyer flasks and adjusting the pH with 0.1 M HCl and/or 0.1 M NaOH. The samples were stirred until no further pH change was observed. Again, the samples were used within 2 days to avoid hydrolysis effects.

A typical experiment consisted of pipetting 3 mL of a sample of known pH, ionic strength and humic/fulvic acid concentration into a fluorescence cell containing a micro stir bar and recording the absorbance and fluorescence intensities at the excitation/emission wavelengths for perylene and rhodamine 110. These values reflect the background intensities of solution components. The sample was then spiked with 10 μL of the combined perylene-rhodamine 110 stock solution and was immediately placed in the stirring module of the spectrophotometer. While mixing, the lid to the sample compartment was closed to prevent photodegradation.

After 3 minutes, the cell was placed in the spectrofluorophotometer and a fluorescence measurement for perylene was made. The sample was then returned to

the spectrophotometer for an absorbance measurement and further mixing. This procedure was repeated for a total elapsed time of 40 minutes. When the rate of change of perylene fluorescence intensity decreased sufficiently (after 20 minutes), fluorescence measurements were made for rhodamine 110 as well.

The initial perylene concentration of the samples after spiking was nominally 0.4 μg/L (1.6 nM) while the rhodamine 110 concentration was nominally 0.1 μg/L (0.27 nM). In order to account for the slight variation in spiking volume among the different samples, the corrected perylene fluorescence intensities were normalized by the mean of the corrected rhodamine 110 fluorescence intensities.

Data Treatment. (A) Anthracene and Pyrene. For PAHs which do not sorb to glassware (more specifically, which do not sorb appreciably during the timescale of an experiment), Gauthier et al. (1986) showed the Stern-Volmer equation for static fluorescence quenching of a PAH compound by DOM can be written:

$$\frac{[\,PAH_T\,]}{[\,PAH_d\,]} = \frac{F_0}{F} = (\,1 + K_{oc}\,[\,OC\,]\,) \qquad (2.1)$$

where $[PAH_T]$ is the total PAH concentration, $[PAH_d]$ is the dissolved PAH concentration, F_0 and F are the fluorescence intensities in the absence and presence of DOM, respectively, [OC] is the organic carbon concentration of DOM, and K_{oc} is the carbon-normalized partition coefficient. Therefore, in a plot of the fluorescence ratio versus concentration of DOM, the partition coefficient is determined from the resulting slope.

The treatment above assumes that fluorescence of the PAH associated with DOM is totally quenched (i.e., that the quantum yield, ϕ, of the complex is zero). Backhus and Gschwend (1990) showed that if the fluorescence is not totally quenched, than the observed fluorescence is described by:

$$\frac{F}{F_0} = \frac{1 + \phi K_{oc}[OC]}{1 + K_{oc}[OC]} \qquad (2.2)$$

With this formulation, they showed that as [OC] $\rightarrow \infty$, the normalized fluorescence asymptotically approaches ϕ. A K_{oc} can be obtained from the curve as the value of $[OC]^{-1}$ at the point where $F/F_0 = (1 + \phi)/2$.

(B) Perylene. For very hydrophobic PAHs which sorb to inorganic surfaces, an alternative approach must be used. Now, not only will the decrease in observed fluorescence be caused by DOM quenching, but also by the sorption of PAH to glassware. Assuming first-order kinetics, Backhus and Gschwend (1990) derived the following equation to describe fluorescence versus time:

$$F = \frac{k_{-w} F_0^*}{k_w + k_{-w}} + \frac{k_w F_0^*}{k_w + k_{-w}} \exp[-(k_w + k_{-w})t] \qquad (2.3)$$

where F_0^* = $[PAH_T]$ - [PAH-OC] at time zero and k_w and k_{-w} are the first-order forward and reverse rate constants for wall adsorption. By fitting equation (2.3) to data and back-extrapolating to t = 0, they obtained the fluorescence values needed for determining partition coefficients with equation (2.2).

RESULTS AND DISCUSSION

Aqueous Chemistry Effects on PAH Partitioning. (A) Anthracene. In the absence of quenchers, a linear relationship between the concentration of anthracene and fluorescence intensity, corrected for the inner-filter effect (Parker, 1968; Lloyd, 1981; Gauthier et al., 1986), was observed over the concentration range studied (0 to 50 μg/L). Neither volatilization nor loss of anthracene to cell walls was detected during the time interval of the measurements.

The fluorescence emission and excitation spectra and the absorbance spectrum for anthracene are shown in Figure 1. The wavelengths used for obtaining the respective fluorescence spectra are listed in Table I. The peak locations and relative heights shown in Figure 1a are similar to published fluorescence spectra (Miller, 1981; Berlman, 1971). The anthracene appears to be free of impurities, as seen by comparing the fluorescence excitation spectrum with the absorbance spectrum (Figure 1b). For a solution with a single solute the corrected or true fluorescence excitation spectrum is identical with, or closely similar to, the absorbance spectrum (Parker, 1968). The presence of extraneous peaks in an absorbance spectrum usually is an indication of impurities. Unfortunately, the spectrofluorophotometer used was not capable of normalizing the excitation intensities and therefore the fluorescence spectra are not corrected. However, although relative peak heights may differ, the location of peaks remains constant for both corrected and uncorrected fluorescence spectra. Therefore, comparison of uncorrected excitation spectra with absorbance spectra can still provide information

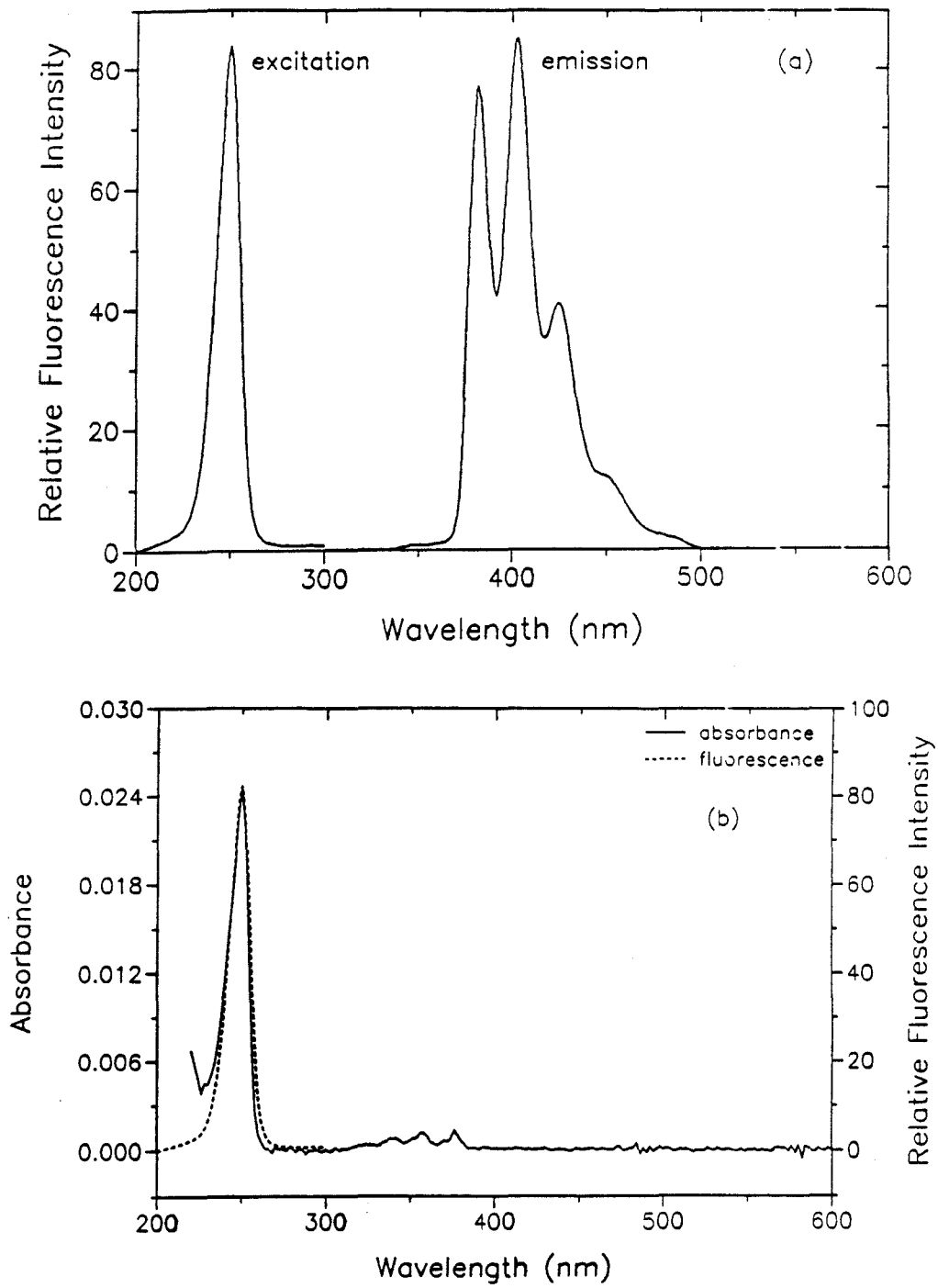


Figure 1. Fluorescence and absorbance spectra of anthracene in water. Nominal anthracene concentration is 40.5 μg/L (0.23 μM). a) Relative fluorescence spectra. b) Absorbance and relative fluorescence excitation spectra.

about the purity of solutes. The absorbance spectrum of anthracene in Figure 1b shows no extraneous peaks compared to the fluorescence excitation spectrum; the location and relative height of the three small absorbance peaks observed between 325 nm and 375 nm appear in corrected fluorescence excitation spectra which scanned across these wavelengths (Berlman, 1971; Miller, 1981).

Kinetics of the binding reaction between anthracene and DOM are shown in Figure 2a. The binding of anthracene by humic acid was observed to be very fast. Quite often, the reaction appeared to be at equilibrium before the first measurement could be taken, a time interval of approximately 15 to 20 seconds after the addition of humic acid. Complete quenching never took longer than 3 minutes for any of the experiments. The reaction was assumed to be equilibrated when no further change in fluorescence intensity was observed. Because the possibility of additional binding to DOM over much longer periods of time cannot be refuted by this data, the state should be considered an apparent equilibrium only. However, fast equilibration times for the association of PAHs with DOM have been reported by other researchers (McCarthy and Jimenez, 1985; Gauthier et at., 1986; Backhus and Gschwend, 1990).

Fluorescence quenching results from the kinetic study of the binding of anthracene by humic acid were analyzed using equation (2.1). As shown in Figure 2b, the observations agree fairly well with the Stern-Volmer equation for static quenching, despite the fact that different samples were utilized to obtain the data in lieu of titrating a single sample with humic acid. Caution must be used in attempting to determine a partition coefficient from this data. Because less than 6 percent of the

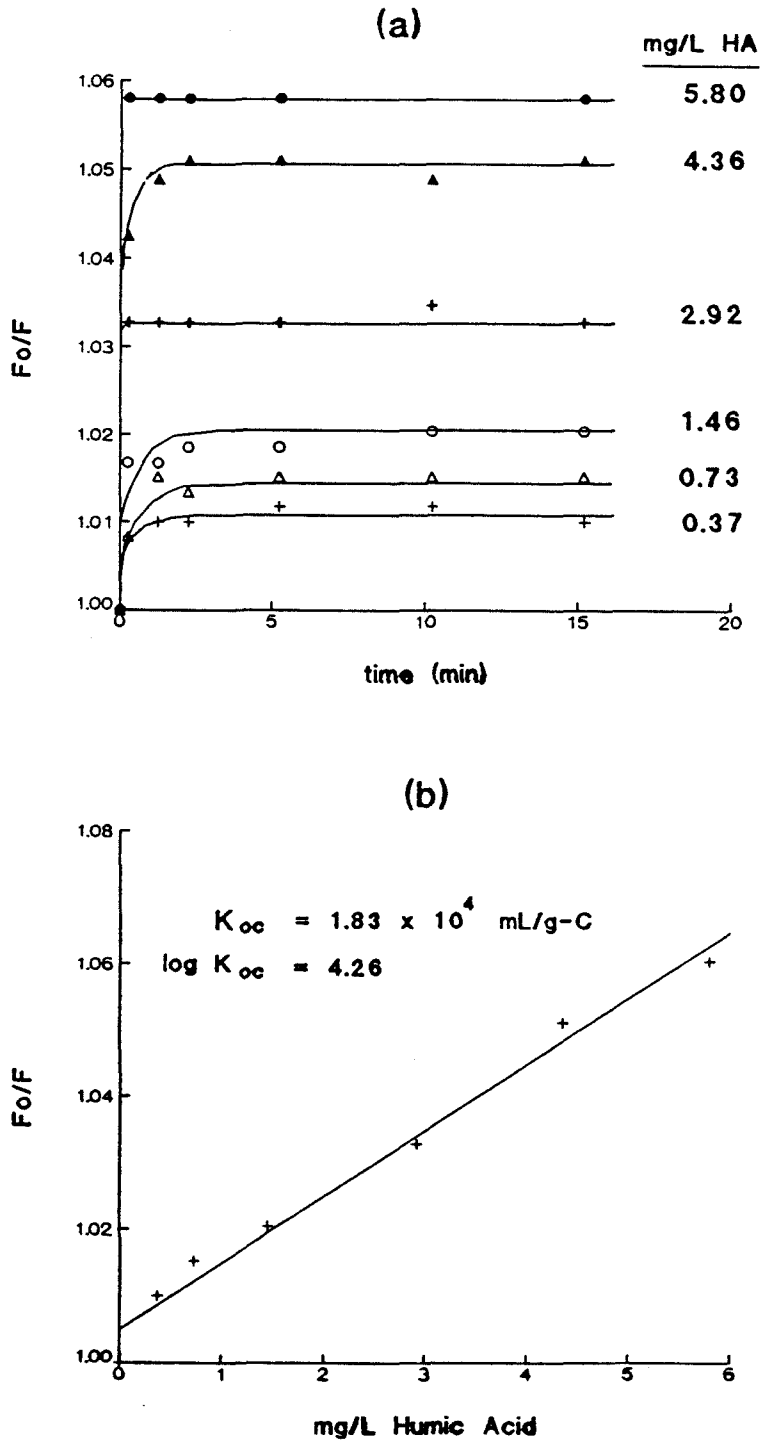


Figure 2. Kinetics of anthracene binding by humic acid in 0.1 M NaCl solution at pH 5. Anthracene concentration is 21.5 μg/L (0.12 μM). a) Binding versus time. b) Stern-Volmer plot.

anthracene initially present was ultimately associated with humic acid, the apparent linearity of F_0/F with respect to humic acid concentration may be misleading over the limited concentration range examined (see Quenching Efficiency in Discussion). Likewise, fitting of the data using equation (2.2) to determine the partition coefficient and quantum yield of the anthracene-humic acid complex is not warranted for the small fractional decrease in fluorescence observed.

The effects of pH, ionic strength and the presence of calcium (1 mM) on the binding of anthracene by dissolved fulvic or humic acid are summarized in Figures 3 and 4, respectively. All partition coefficients were determined using equation (2.1) to analyze titrations of anthracene solutions with fulvic or humic acid.

In Figure 3a, changes in pH are seen to have a modest effect on the binding of anthracene by fulvic acid. As the pH is increased, only a slight decrease in the partition coefficient is observed for the NaCl solutions of various ionic strengths. For the same pH increase, the solutions with 1 mM Ca^{2+} (0.1 M total ionic strength) show a slight increase in the partition coefficient. In order to observe the ionic strength effects more clearly, the partition coefficient was plotted as a function of ionic strength in Figure 3b. Regardless of the pH, an increase in ionic strength resulted in a small decrease in the binding of anthracene by fulvic acid in NaCl solutions. For the solutions with 1 mM Ca^{2+} and 0.1 M total ionic strength, the results were mixed. At pH 4 the presence of Ca^{2+} decreased the amount of binding compared to the NaCl solutions of equal ionic strength, while at pH 7 and 10 it caused a moderate increase in the partition coefficient relative to the NaCl solutions.

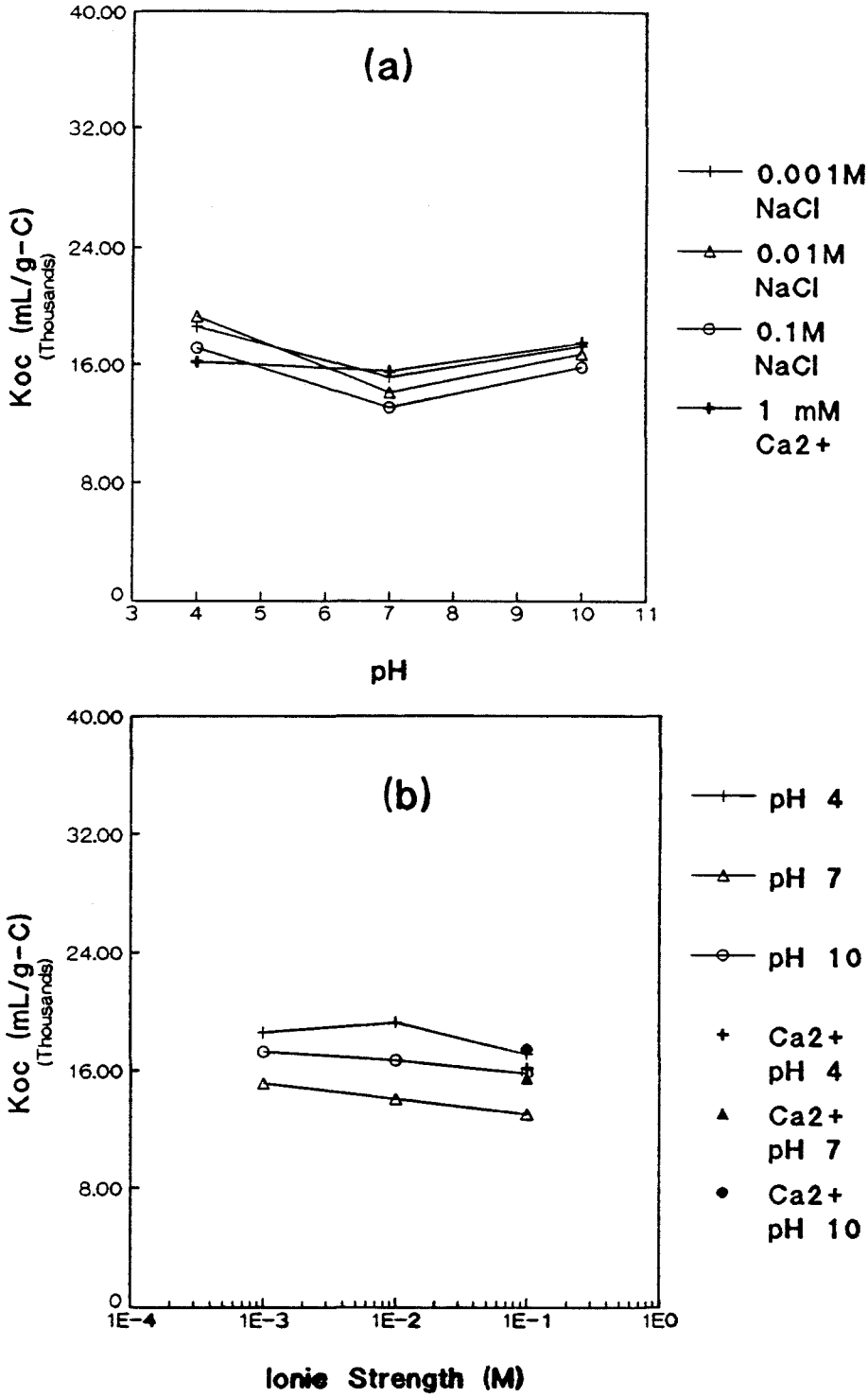


Figure 3. Binding of anthracene by fulvic acid. Data for 1 m$\underline{M}$ Ca^{2+} are at a total ionic strength of 0.1 $\underline{M}$. a) K_{oc} versus pH. b) K_{oc} versus ionic strength. Symbols connected by lines refer to NaCl solutions. Single (**bold**) points refer to experiments with 1 m$\underline{M}$ Ca^{2+} at the appropriate pH values.

The aqueous chemistry effects were more significant for the anthracene-humic acid complexes. As shown in Figure 4a, an increase in pH resulted in a slight increase in the partition coefficient for the 0.1 M ionic strength solutions with 1 mM Ca^{2+}, relatively little change for the 1 mM NaCl solutions, a modest decrease in the partition coefficient for the 10 mM NaCl solutions, and a much larger decrease for the 0.1 M NaCl solutions. The importance of varying ionic strength is shown in Figure 4b. For the NaCl solutions at pH 7 and 10, an increase in ionic strength resulted in a decrease in the binding of anthracene by humic acid while the opposite trend was observed for the pH 4 NaCl solutions. The presence of 1 mM Ca^{2+} in the 0.1 M ionic strength solutions had a similar effect as was seen for fulvic acid. At pH 4 the humic acid solutions with Ca^{2+} showed a decreasing ability to bind anthracene relative to the NaCl solutions of the same ionic strength. However, humic acid in the presence of Ca^{2+} in the pH 7 solutions and, especially, the pH 10 solutions was better able to bind anthracene relative to the NaCl solutions.

(B) Pyrene. The fluorescence emission and excitation spectra (obtained using the wavelengths listed in Table I) and absorbance spectrum of pyrene are shown in Figure 5. The fluorescence spectra (Figure 5a) are similar to those in Berlman (1971) and Miller (1981). A comparison of the fluorescence excitation spectrum with the absorbance spectrum (Figure 5b) shows the pyrene solution to be free of impurities, as evidenced by the lack of extraneous peaks in the absorbance spectrum. The difference in relative heights of the peaks in the two spectra is an artifact of the uncorrected fluorescence excitation intensities.

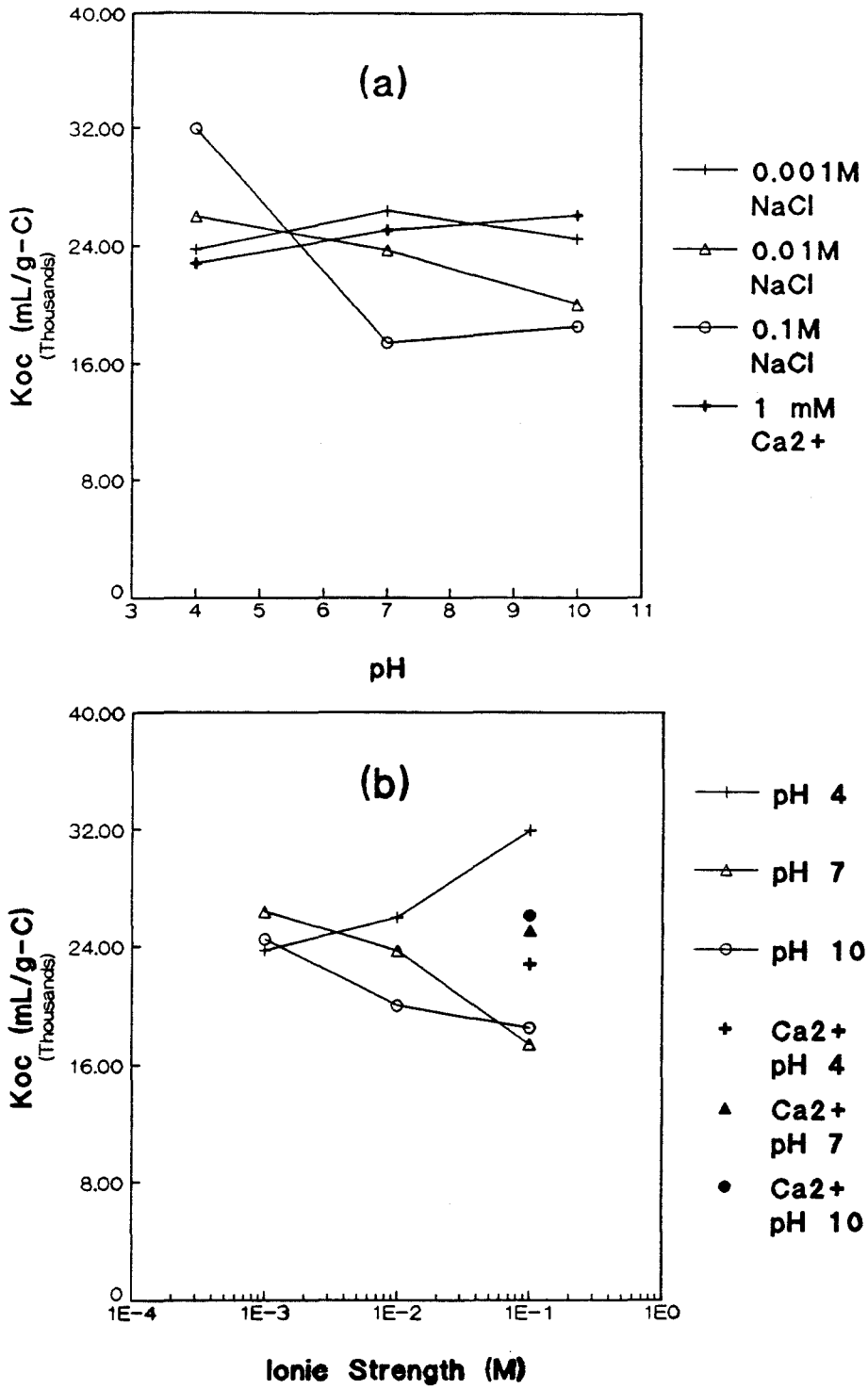


Figure 4. Binding of anthracene by humic acid. Data for 1 mM Ca^{2+} are at a total ionic strength of 0.1 M. a) K_{oc} versus pH. b) K_{oc} versus ionic strength. Symbols connected by lines refer to NaCl solutions. Single (**bold**) points refer to experiments with 1 mM Ca^{2+} at the appropriate pH values.

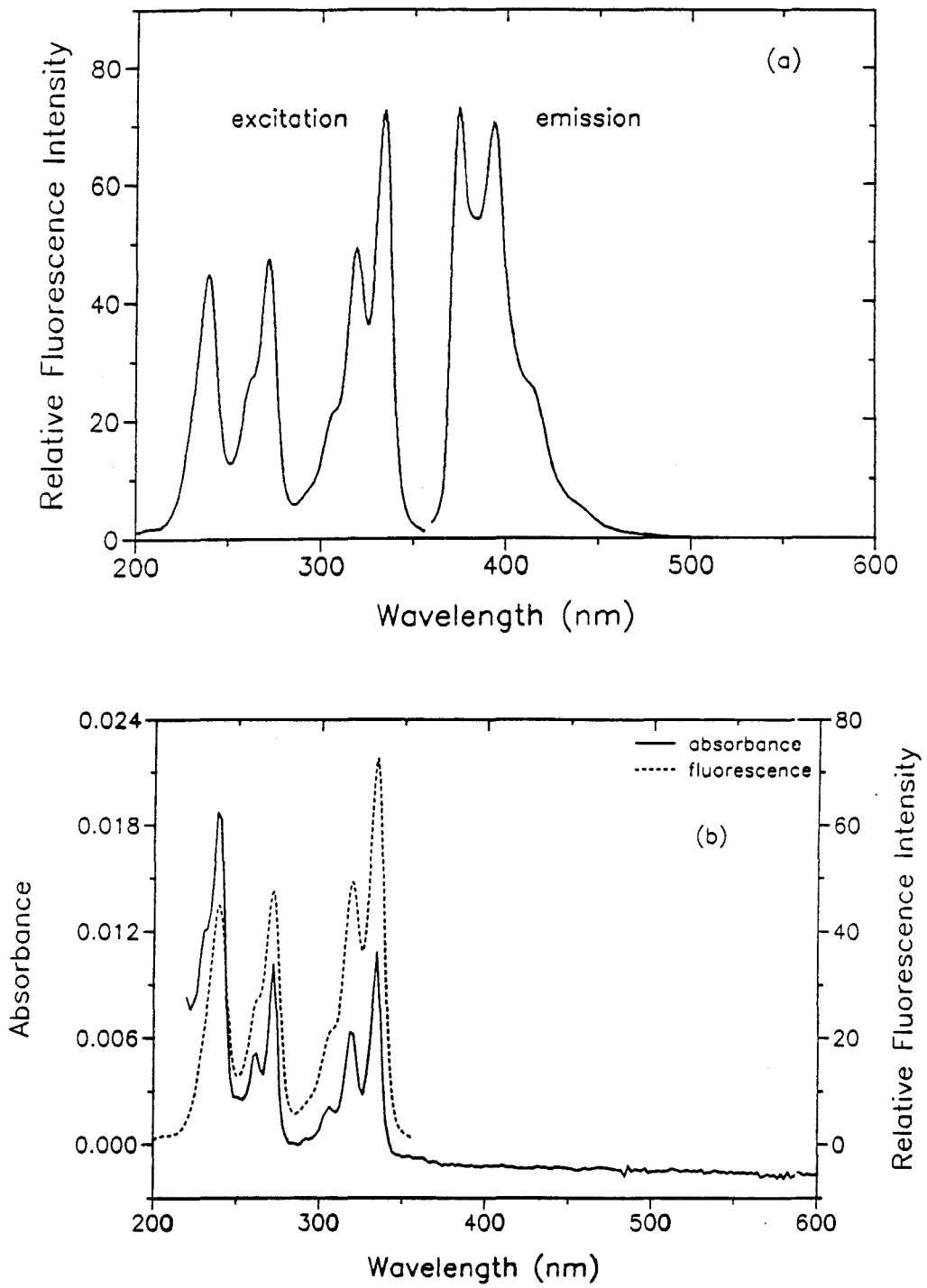


Figure 5. Fluorescence and absorbance spectra of pyrene in water. Nominal pyrene concentration is 83.4 μg/L (0.41 μM). a) Relative fluorescence spectra. b) Absorbance and relative fluorescence excitation spectra.

Figure 6a shows the kinetics of pyrene binding to humic acid. As seen previously for anthracene, the binding reaction between pyrene and humic acid is very fast. Most of the reactions appeared to be equilibrated before the first measurement could be taken, approximately 20 seconds after the addition of humic acid. Analysis of the data with equation (2.1) shows good agreement with the Stern-Volmer relationship (Figure 6b). Again, however, care must be taken in determining a partition coefficient from this data since only a maximum of 15 percent of the total pyrene is bound by the humic acid.

In the pyrene-fulvic acid system, changes in the aqueous chemistry had more of an effect on partitioning than was seen for anthracene-fulvic acid. An increase in pH from 4 to 7 resulted in a decrease in the partition coefficients for all NaCl solutions (Figure 7a); however, a further increase in pH from 7 to 10 had no effect on the amount of binding. The Ca^{2+} solutions showed an initial decrease in the binding of pyrene by fulvic acid followed by a subsequent increase as the pH increases from 4 to 10. At constant pH values, an increase in ionic strength for the NaCl solutions resulted in decreases in the binding of pyrene by fulvic acid (Figure 7b). The presence of 1 m$\underline{M}$ Ca^{2+} in the 0.1 $\underline{M}$ total ionic strength solutions had a similar effect to that observed for anthracene. At pH 4, Ca^{2+} had little effect on the partition coefficient relative to the NaCl solutions, while at pH 7 and, in particular, pH 10 it resulted in an increase in the partition coefficient.

In the absence of Ca^{2+}, the binding of pyrene by humic acid showed similar trends to those for the pyrene-fulvic acid system (Figure 8). Only for the solutions

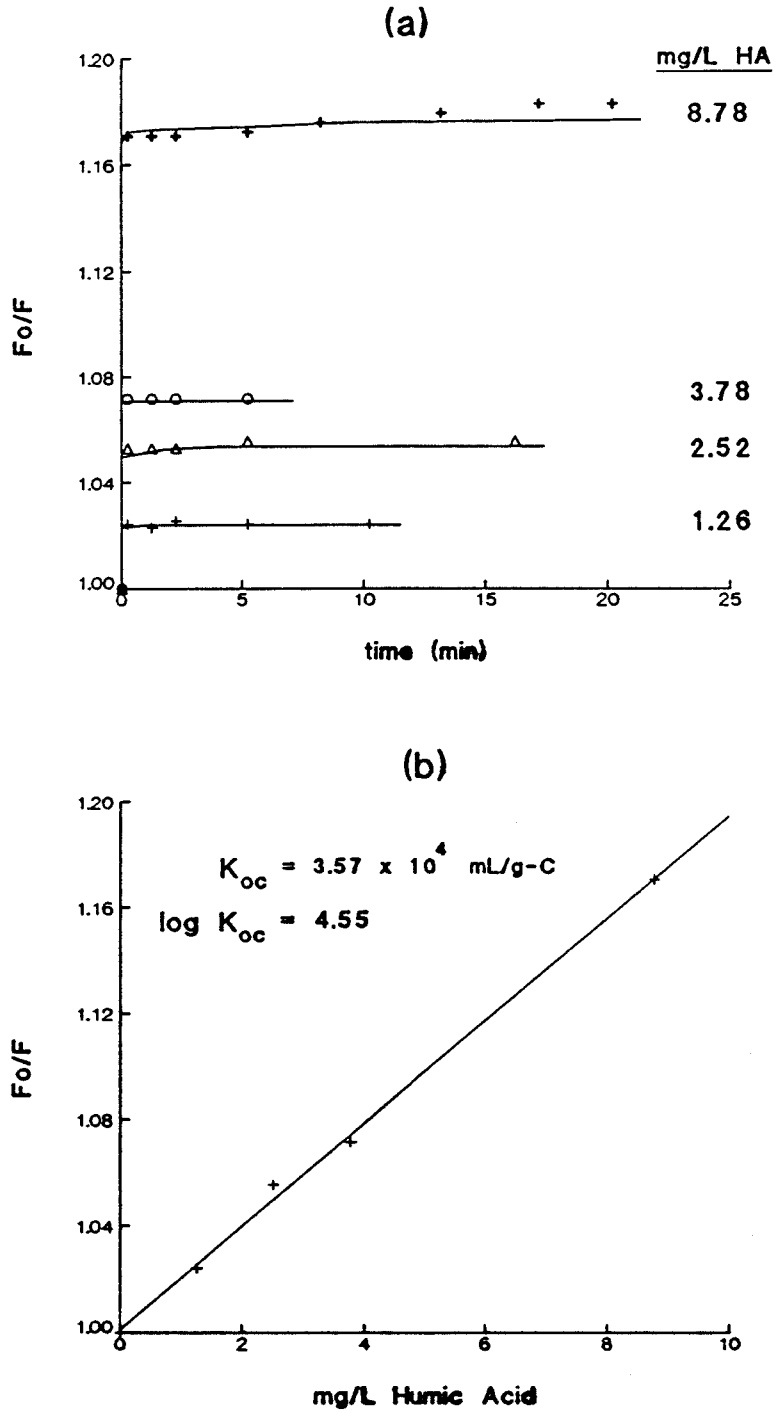


Figure 6. Kinetics of pyrene binding by humic acid in 0.1 M NaCl solution at pH 3. Pyrene concentration is 83.4 μg/L (0.41 μM). a) Binding versus time. b) Stern-Volmer plot.

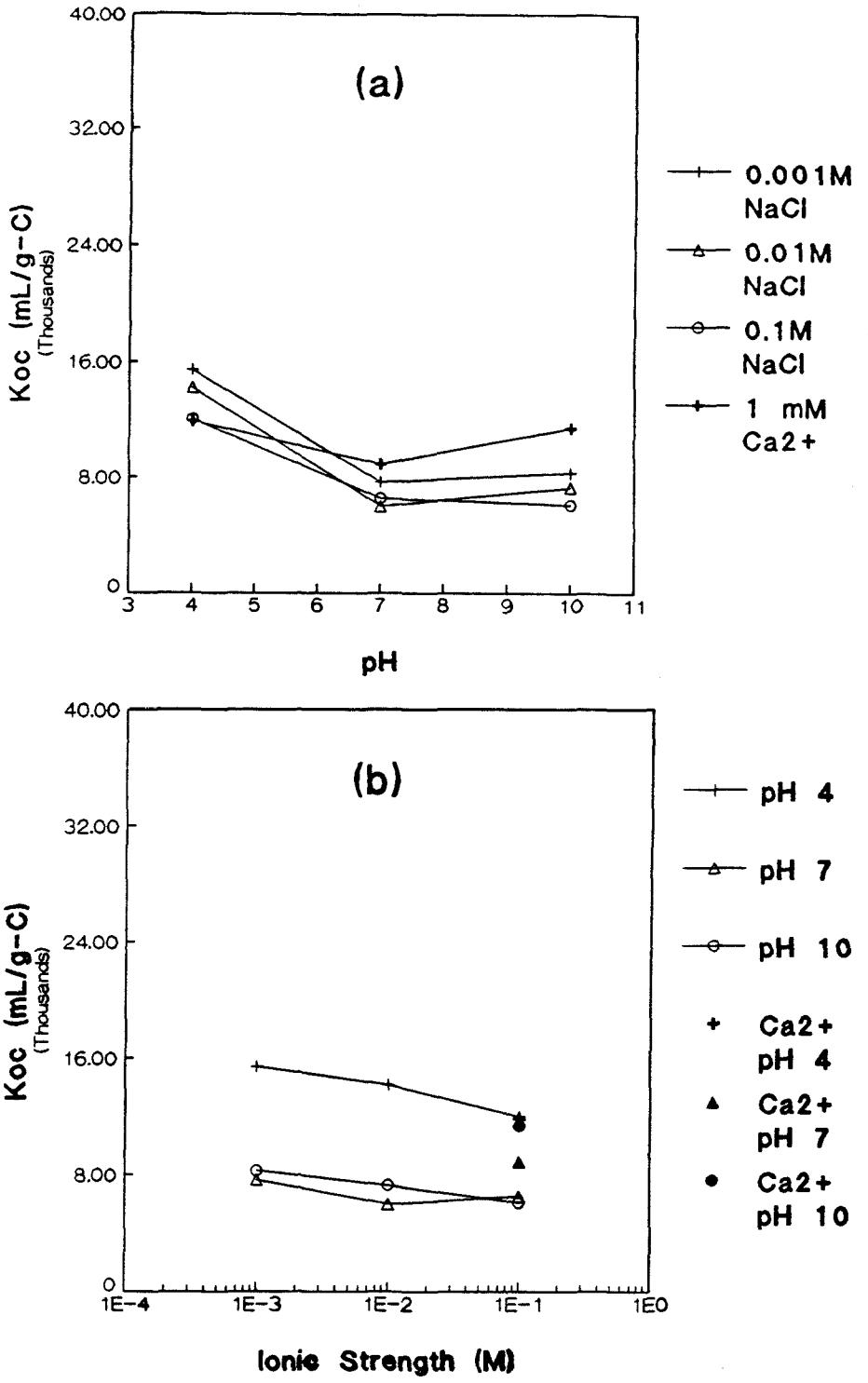


Figure 7. Binding of pyrene by fulvic acid. Data for 1 mM Ca^{2+} are at a total ionic strength of 0.1 M. a) K_{oc} versus pH. b) K_{oc} versus ionic strength. Symbols connected by lines refer to NaCl solutions. Single (**bold**) points refer to experiments with 1 mM Ca^{2+} at the appropriate pH values.

with Ca^{2+} present was a significant difference observed. In Figure 8a, the partition coefficient decreases uniformly for the Ca^{2+} solutions as the pH increases from 4 to 10. The presence of Ca^{2+} had no effect on the binding of pyrene by humic acid at pH 10, while at pH 4 and 7 the trends are similar to those previously observed (Figure 8b).

(C) Perylene. The fluorescence excitation and emission spectra of perylene, using the wavelengths listed in Table I, are shown in Figure 9a for a typical aqueous sample which contains both perylene and rhodamine 110 (0.4 μg/L and 0.1 μg/L, respectively). A comparison with published fluorescence spectra of perylene (Berlman, 1971; Miller, 1981) shows good agreement. Because the published fluorescence spectra were obtained using organic solvents (e.g., cyclohexane), higher concentrations of perylene could be used and more structure is observed. For example, peaks located at approximately 384 nm and 504 nm appear as shoulders in Figure 9a. Another potential complication in comparing spectra obtained using different solvents arises from Raman scattering. Peaks resulting from the Raman scattering of water were observed at 405 nm and 506 nm and had to be subtracted in order to obtain the perylene spectra shown in Figure 9. The good agreement with published spectra obtained using only perylene solutions confirms that the fluorescence signal of rhodamine 110 does not interfere with that of perylene at the wavelengths used.

Further confirmation of the absence of signal interference between perylene and rhodamine 110 can be seen in Figure 9b, which compares the fluorescence

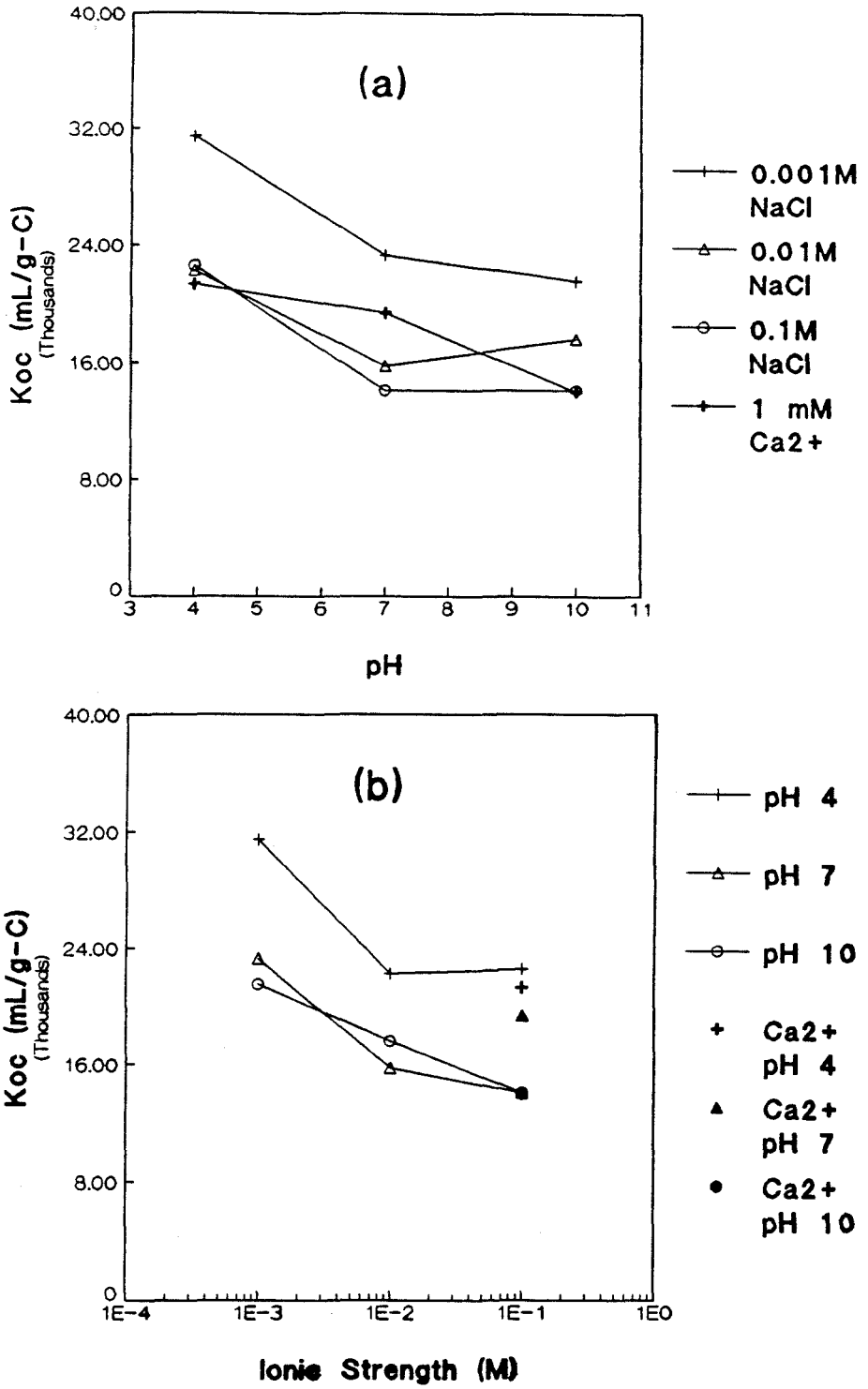


Figure 8. Binding of pyrene by humic acid. Data for 1 m<u>M</u> Ca^{2+} are at a total ionic strength of 0.1 <u>M</u>. a) K_{oc} versus pH. b) K_{oc} versus ionic strength. Symbols connected by lines refer to NaCl solutions. Single (**bold**) points refer to experiments with 1 m<u>M</u> Ca^{2+} at the appropriate pH values.

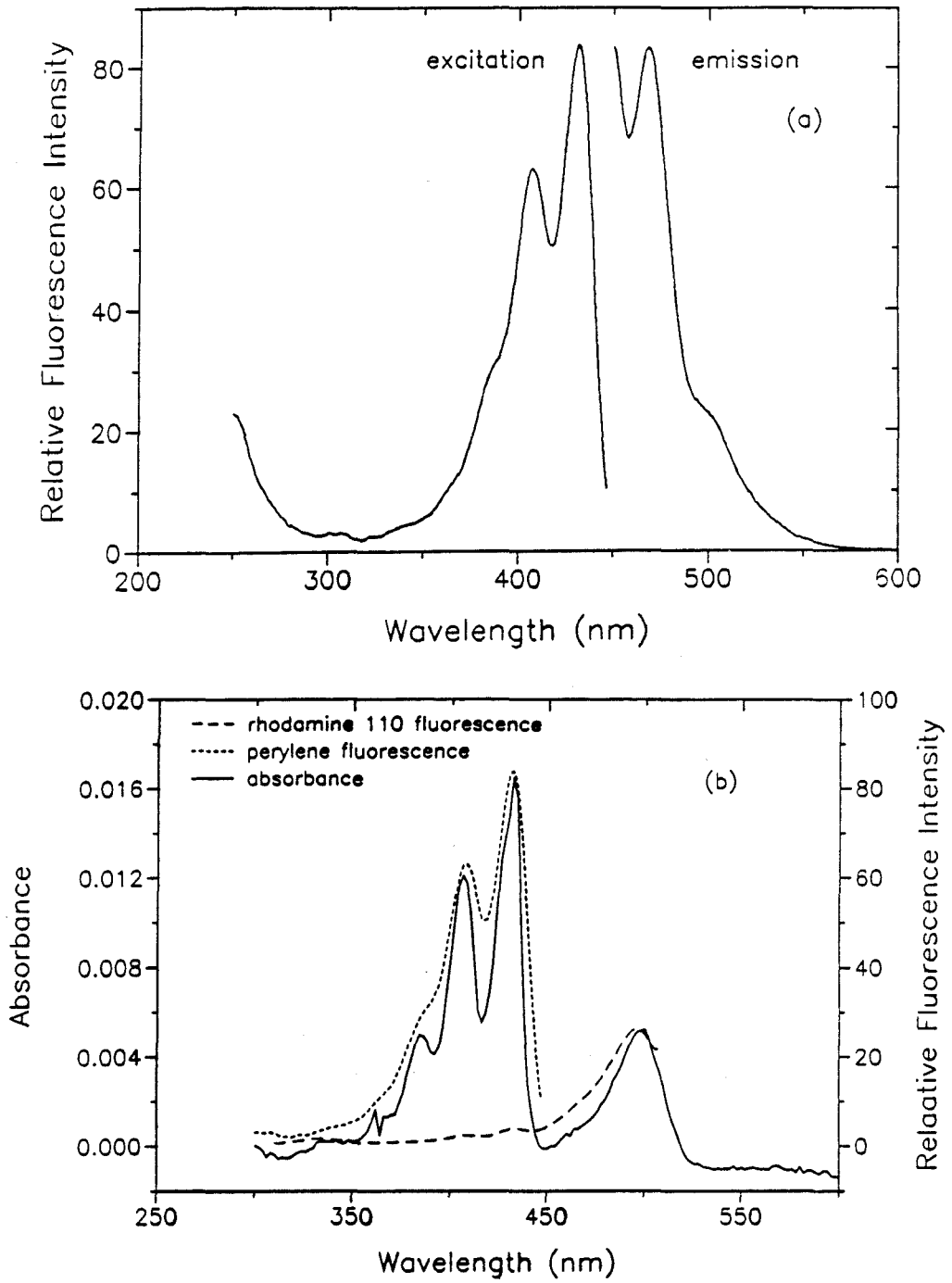


Figure 9. **Fluorescence and absorbance spectra of perylene.** a) Relative fluorescence spectra of perylene in aqueous solution. Nominal perylene concentration is 0.4 μg/L (1.6 nM). b) Relative fluorescence excitation spectra of perylene (0.4 μg/L) and rhodamine 110 (0.1 μg/L) in aqueous solution and an absorbance spectrum of perylene (120 μg/L) and rhodamine 110 (30 μg/L) in methanol.

excitation spectra of perylene and rhodamine 110 with the absorbance spectrum of a sample containing both solutes. The fluorescence spectra are from an aqueous sample, while a methanol solution (120 μg/L perylene, 30 μg/L rhodamine 110) was used to obtain the absorbance spectrum. Absorbance could not detect the low concentrations of perylene and rhodamine 110 in the aqueous sample, demonstrating the relative sensitivity of fluorescence. The perylene peak at 384 nm can now be seen in the absorbance spectrum. Also, the fluorescence excitation scan of rhodamine 110 shows the minimal interference it receives from the presence of perylene in the aqueous solution.

Using the fluorescence quenching method of Backhus and Gschwend (1990), the rate at which perylene partitions between water and DOM is observed indirectly and, in a sense, must be known a priori in order that the loss of perylene from aqueous solution can be resolved into perylene binding by DOM versus the adsorption of perylene to glassware. A key assumption of the method is that the rate of PAH binding to DOM is fast relative to the rate of PAH adsorption to the cell walls. By allowing the partitioning reaction to reach equilibrium before the initial measurement is taken, subsequent decreases in fluorescence can then be attributed to adsorption of the PAH to cell walls. In the presence and absence of DOM, measurements of the perylene fluorescence intensity decreased exponentially with time, in accordance with equation (2.3). The distinct and parallel curves obtained for various concentrations of DOM (e.g., Figure 10a for perylene-humic acid) indicate that the binding of perylene by DOM was complete within 3 minutes, the time

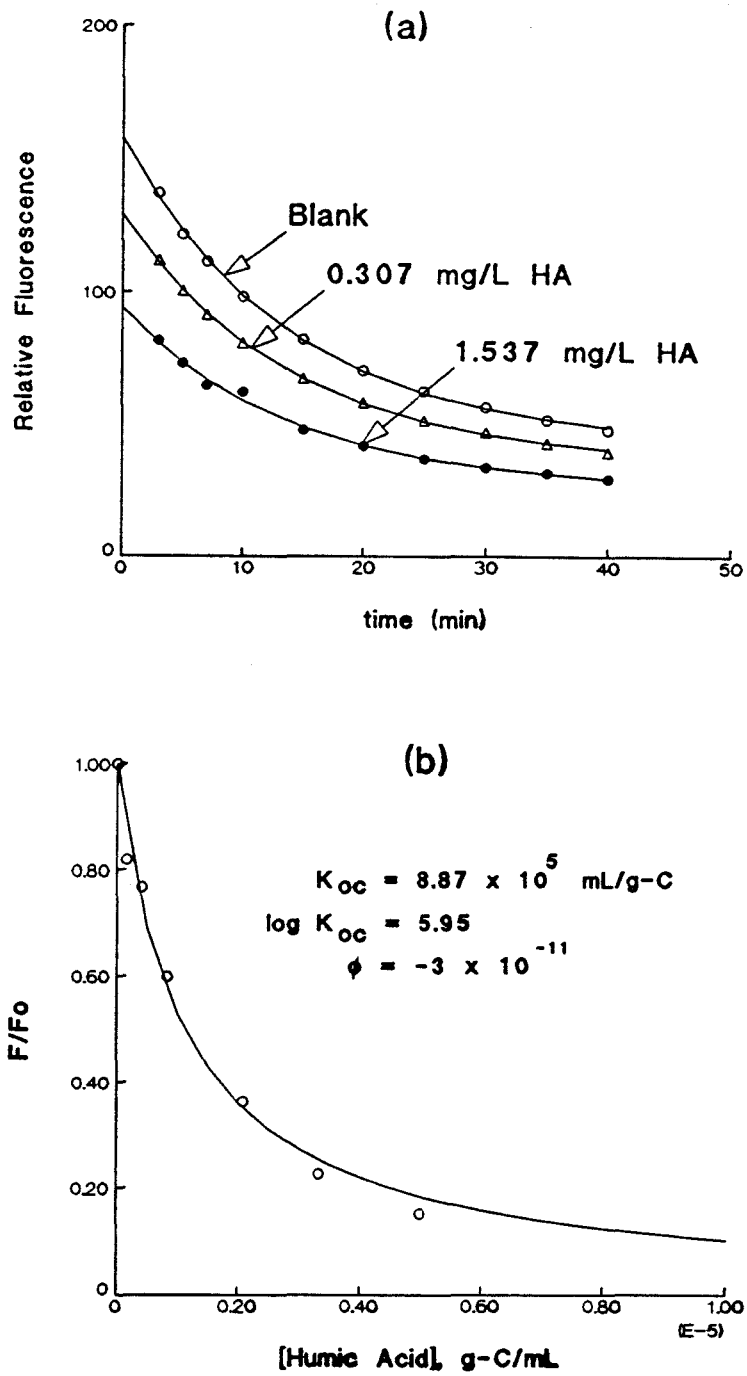


Figure 10. Perylene binding by humic acid in 0.1 M NaCl solutions at pH 4. Nominal perylene concentration for each sample is 0.4 μg/L (1.6 nM). a) Adsorption of perylene to cell walls versus time. b) Determination of K_{oc} and ϕ.

allotted before taking the first measurement.

A nonlinear least-squares curve-fitting program was used to fit equation (2.3) to the measured fluorescence intensities. The fluorescence values (after accounting for wall losses) were then analyzed using equation (2.2) to determine partition coefficients and quantum yields for the perylene-DOM complexes. Results for a typical experiment are shown in Figure 10b, in which the normalized fluorescence intensities obtained from back-extrapolation to t = 0 are plotted as a function of DOM concentration. All curves obtained for the various perylene-DOM systems asymptotically approached quantum yields of zero as [OC] $\rightarrow \infty$.

The aqueous chemistry effects on the partitioning of perylene to DOM are summarized in Figure 11. Only a few experiments were performed with fulvic acid because of its lower ability to bind perylene and its apparent insensitivity to aqueous chemistry changes relative to humic acid. All partition coefficients were determined using the method described above.

As the pH increases from 4 to 10 for a constant ionic strength, a decrease in the binding of perylene is observed for all of the samples (Figure 11a). The presence of Ca^{2+} (1 mM) had little effect on the partition coefficient when compared to NaCl solutions of the same ionic strength. Increases in the ionic strength from 1 mM to 0.1 M caused a decrease in the partition coefficients for humic acid regardless of pH (Figure 11b). Fulvic acid at pH 4, however, showed little dependence on the ionic strength as only a barely perceptible decrease in the partition coefficient is observed with increasing ionic strength. The effects of Ca^{2+} on the binding of perylene by

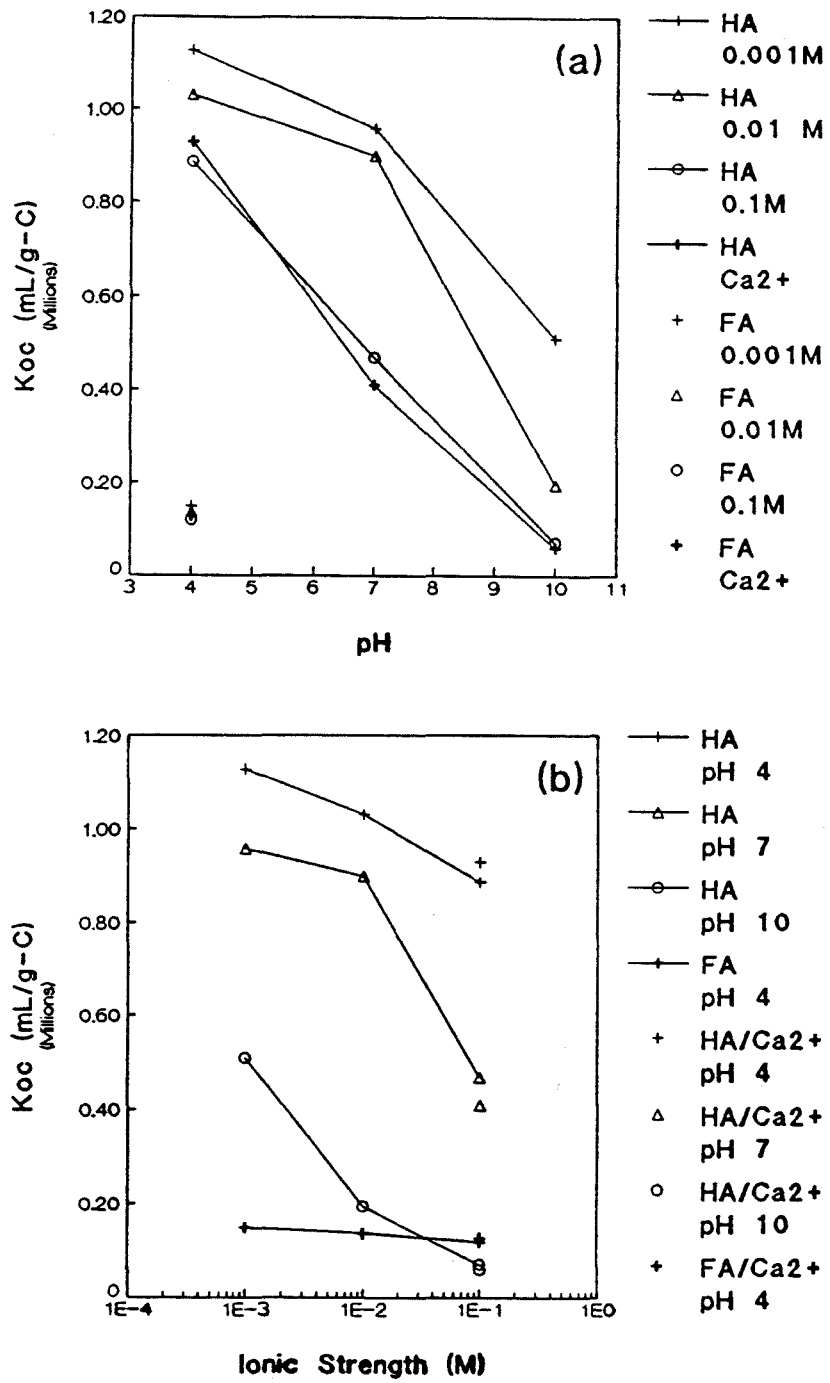


Figure 11. Binding of perylene by humic and fulvic acid. Data for 1 mM Ca^{2+} are at a total ionic strength of 0.1 M. a) K_{oc} versus pH. Symbols connected by lines are experiments with humic acid. Single points at pH 4 refer to experiments with fulvic acid. b) K_{oc} versus ionic strength. Symbols connected by lines are experiments in NaCl solutions. Single points at 0.1 M ionic strength refer to experiments with 1 mM Ca^{2+}.

DOM, while small, are opposite to the trends seen previously for anthracene and pyrene. The presence of Ca^{2+} at pH 7 and 10 decreases the ability of humic acid to bind perylene, while both humic and fulvic acid show a slight increase in the partition coefficient at pH 4.

Binding of HOC by Humic Substances. (A) Mechanism. The association of nonpolar organic pollutants with the organic carbon of sediments and soils had typically been considered a surface adsorption process until Lambert (1967) proposed that the association was better described as liquid-liquid phase equilibrium. This concept has gained widespread acceptance in recent years, particularly by Chiou and coworkers (e.g., Chiou et al., 1979, Kile and Chiou, 1989). They argue that an HOC-organic material dissolution process is supported by a number of observations:

(a) Binding isotherms are linear up to the limit of solute saturation in the aqueous phase, with no apparent curvature at the higher concentrations. Adsorption models usually predict a maximum saturation condition.

(b) Competitive effects by binary solutes are not observed in these systems. Adsorption reactions usually show competitive effects because of the constraint of available surface area and/or specific sites.

(c) Partition coefficients normalized by f_{oc} for nonionic organic compounds are highly correlated with their hydrophobicity, as measured by K_{ow}, octanol-water partition coefficients, or S^{-1}, inverse aqueous solubilities. Plots of log K_{oc} versus log S have been observed to be linear over seven orders of magnitude of aqueous solubility.

(d) Small temperature effects are observed for solute binding. The equilibrium heat for solute dissolution is relatively small and constant because of the partial cancellation of heats of solution for transfer of solute from water to the organic phase. Adsorption reactions generally are highly exothermic, which offset the decrease in solute entropy upon adsorption.

Kile and Chiou (1989) substantiated the last argument by calculating the molar enthalpy value for the binding of DDT with dissolved humic acid observed by Carter and Suffet (1983). Kile and Chiou (1989) reasoned that an equilibrium partition (dissolution) coefficient should be less sensitive to temperature than an equilibrium adsorption coefficient for the reasons stated above. The binding constant of DDT showed a nearly twofold increase when the temperature was decreased from 25 to 9° C. Using the van't Hoff equation, Kile and Chiou (1989) determined the molar enthalpy value to be approximately -21 kJ mol^{-1}. Because this value is much less than the molar heat of condensation from water for DDT (-39 kJ mol^{-1}), they argued that the association of DDT with humic material was not mechanistically consistent with surface adsorption.

Further corroboration of the relatively small temperature effects for organic pollutant binding to DOM is found in Traina et al. (1989). They attempted to refute a dynamic quenching mechanism by observing the temperature dependence of fluorescence for naphthalene-DOM complexes. After a two hour equilibration at 25° C, samples were subjected to two heating and two cooling cycles over a range from 1 to 75° C. A total of 32 measurements per sample were made during the study.

No apparent temperature dependence was observed for the fluorescence ratio F_0/F. They concluded that dynamic quenching was not present in their system, because a diffusion-controlled process should show a dependence on temperature.

Traina et al. (1989) claimed that the absence of temperature effects in their system did not indicate that association of naphthalene with DOM was independent of temperature, because they equilibrated the solutions initially at 25° C. However, during the cycling of each sample, fluorescence intensities were measured 15 minutes after the circulating water bath had stabilized at the desired temperature. This indicates that the total time required for each sample experiment was a minimum of 8 hours, and possibly much more, depending on the time required for the water bath to stabilize at each new temperature. It is likely that their system reached a new equilibrium for each temperature examined (e.g., see Kinetics of Partitioning section below). Therefore, an alternative explanation for their results is that the binding of naphthalene by DOM was relatively insensitive to temperature because the mechanism was driven by entropy effects (i.e., the hydrophobic interaction).

It should be noted that the macroscopic physical model for association of nonpolar organic compounds with natural organic material is still a matter of debate (Caron and Suffet, 1989). Most researchers avoid the controversy by loosely describing their observations as "sorption" phenomena, without regard to the fundamental, molecular-level mechanisms of the process. The term partitioning is used frequently in this work because it is an adequate macroscopic concept to describe hydrophobic interactions. It is doubtful, however, if either adsorption models

or dissolution models will ultimately be able to describe every sorption reaction between nonpolar organic compounds and DOM.

The macroscopic partition interaction envisioned by Chiou and coworkers is analogous to that observed for the solubilization of hydrophobic solutes in micelles (Kile and Chiou, 1989). Surfactant monomers aggregate into micelles in order to remove their hydrophobic entities from contact with water. The hydrocarbon chains in such micelles are regarded as disordered; the hydrophobic core is, in effect, a small volume of liquid hydrocarbon almost completely devoid of water (Tanford, 1980; Israelachvili, 1985). This was elegantly verified by the work of Kalyanasundaram and Thomas (1977), in which pyrene was used as a photophysical probe of sodium dodecyl sulfate micelles. They observed that the polarity of the micelle core was approximately equivalent to that of benzene. Whether DOM can form similar "microscopic organic environments" is not presently known.

Several researchers have attempted to describe the association between nonpolar organic molecules and natural organic material on a molecular level. Freeman and Cheung (1981) hypothesized natural organic material in sediments to be a humic-kerogen gel affixed to mineral surfaces. They pictured humic material as highly branched polymer chains forming complex three-dimensional networks. Absorbed liquids would cause the network to swell and form a gel. The binding of organic compounds was envisioned to be a process which incorporates them into the humic gel structure, and thus binding is controlled by the relative affinity of the compounds for the aqueous and gel phases. With these assumptions, Freeman and

Cheung (1981) applied solubility parameter theory to describe the binding processes.

Schnitzer and Khan (1972) proposed that humic material consists of a broken network of poorly condensed aromatic rings with appreciable numbers of disordered aliphatic or alicyclic structures attached around an aromatic core. The building blocks of the humic polymer were thought to be phenolic and benzenecarboxylic acids which were joined by hydrogen bonds and van der Waals forces to form relatively stable polymeric structures. The humic material was thought to have an open structure which allowed for a considerable number of voids of different dimensions and the arrangement was expected to be sensitive to changes in pH, salt concentration and valence of cations. It was hypothesized that the voids could trap organic compounds, provided the compounds had the proper molecular sizes to fit into the holes and the environment in the voids was conducive to association with the organic compounds.

Although the foregoing two "molecular-level" descriptions of association between nonpolar organic compounds and DOM differ, they both require that a favorable (i.e., hydrophobic) environment be present in DOM. Macroscopically, this concept has been referred to as the "quality" of DOM. Studies have indicated that a large variability in the amount of binding of a given organic compound exists for DOM isolated from different sources (Carter and Suffet, 1982; Landrum et al., 1984; Garbini and Lion, 1985). Gauthier et al. (1987) found that the affinity of DOM for pyrene increased as the degree of aromaticity in DOM increased. They hypothesized that the increased affinity resulted because aromatic bonds in DOM would increase

the polarizability of the material and therefore increase the strength of van der Waals attraction forces between pyrene and DOM.

Chiou et al. (1986, 1987) found that the single most important criterion for partitioning of a given solute into DOM was the molecular size of the dissolved organic material. Given that the molecular size was larger than some critical (but unspecified) value, the amount of binding then would be a function of the polarity, configuration and conformation of the DOM. Therefore, a partition interaction would be more effective with a large macromolecule containing regions of large nonpolar volumes.

The aqueous chemistry environment of natural water systems controls to a large extent the polarity and conformation of DOM (Schnitzer and Kodama, 1975; Ghosh and Schnitzer, 1980; Cornel et al., 1986; Leenheer et al., 1989). Intermolecular interactions between humic molecules and intramolecular interactions between functional groups on a molecule change the chemical and physical properties of humic material in different aqueous environments. These interactions control the self-association of, and ultimately, the size, shape and polarity of humic substances. Both nonpolar and polar interactions are thought to be responsible for the self-aggregation of humic material, although the nonpolar interaction is thought to be insignificant for the humic and fulvic acids studied here (Leenheer et al., 1989). However, because both polar intermolecular and intramolecular interactions will increase the nonpolar character of humic substances, increased partitioning of nonpolar contaminants into the humic material may be observed.

Molecular interactions of DOM are dependent on temperature, pH, ionic strength and type of countercations in solution, as well as other chemical parameters (Leenheer et al., 1989). For intermolecular interactions, the concentration of DOM is also important. Because the above parameters are significant for the self-association of humic material, they should also be important for organic pollutant binding by humic substances. However, few studies have been made of the effects of aqueous chemistry on the partitioning of nonpolar organic compounds by DOM. Carter and Suffet (1982) observed a decrease in binding of DDT with humic acid when the pH was raised from 6 to 9.2. Kile and Chiou (1989) reported decreases in the binding of DDT and two PCBs by a soil humic acid and Suwannee River fulvic acid at pH 8.5 relative to pH 6.5. At pH values below 6.5, however, the partitioning with fulvic acid did not show any dependence on pH. Traina et al. (1989) studied the effects of pH, ionic strength and cation type on the partitioning of naphthalene by a poorly-characterized muck soil organic matter extract. They observed neither pH (pH 1.5 to 7.3) nor ionic strength (0.05 to 0.5 M) effects in the binding of naphthalene. The presence of Al^{3+}, however, appeared to decrease the binding of naphthalene relative to Na^{+} and Ca^{2+}, although variations in pH complicate interpretation of their results.

(B) Thermodynamics of Partitioning. Values for the carbon-normalized partition coefficients for humic and fulvic acid with different PAH solutes and varying aqueous chemistry conditions are listed in Table V. The partition coefficients for anthracene and pyrene were determined using both equations (2.1) and (2.2). The

Table V. Experimental Partition Coefficients and Quantum Yields.[a,b]

		Anthracene			Pyrene			Perylene	
		K_{oc} [c] ($\times 10^{-4}$)	K_{oc} [d] ($\times 10^{-4}$)	ϕ ($\times 10^{6}$)	K_{oc} [c] ($\times 10^{-4}$)	K_{oc} [d] ($\times 10^{-4}$)	ϕ ($\times 10^{6}$)	K_{oc} [d] ($\times 10^{-5}$)	ϕ ($\times 10^{12}$)
0.001M NaCl									
pH 4	HA	2.373	2.233	5	3.147	3.033	4	11.279	(4)
	FA	1.854	1.787	7	1.542	1.558	7	1.494	600
pH 7	HA	2.636	2.696	4	2.331	2.344	5	9.582	< 1
	FA	1.509	1.444	9	0.766	0.717	20	ND[e]	ND[e]
pH 10	HA	2.448	2.319	6	2.154	2.198	5	5.096	(2)
	FA	1.724	1.668	7	0.828	0.787	20	ND	ND
0.01M NaCl									
pH 4	HA	2.596	2.466	5	2.226	2.179	6	10.314	1
	FA	1.927	1.786	5	1.420	1.449	8	1.374	70
pH 7	HA	2.370	2.325	5	1.575	1.449	9	8.991	(< 1)
	FA	1.406	1.264	8	0.598	0.568	20	ND	ND
pH 10	HA	2.002	1.818	7	1.761	1.747	7	1.946	< 1
	FA	1.670	1.490	8	0.729	0.690	20	ND	ND
0.1M NaCl									
pH 4	HA	3.194	2.771	4	2.259	2.351	5	8.869	(30)
	FA	1.712	1.602	7	1.201	1.206	10	1.194	90
pH 7	HA	1.740	2.146	5	1.407	1.646	7	4.689	< 1
	FA	1.305	1.232	10	0.651	0.655	20	ND	ND
pH 10	HA	1.852	2.078	5	1.408	1.282	8	0.716	2
	FA	1.581	1.427	9	0.609	0.606	20	ND	ND
1mM Ca^{2+} [f]									
pH 4	HA	2.280	2.302	5	2.133	2.229	5	9.292	< 1
	FA	1.616	1.556	8	1.187	1.234	10	1.276	70
pH 7	HA	2.505	2.423	5	1.937	1.997	6	4.096	< 1
	FA	1.549	1.525	8	0.888	0.911	10	ND	ND
pH 10	HA	2.609	2.555	5	1.398	1.344	10	0.601	20
	FA	1.746	1.633	8	1.139	1.167	10	ND	ND

[a] Units of K_{oc} are mL/g-C. (ϕ) denotes negative value. [b] HA, humic acid. FA, fulvic acid. [c] Equation (2.1). [d] Equation (2.2). [e] ND, not determined. [f] 0.1 M total ionic strength.

two equations gave similar K_{oc} values, suggesting that the second fitting parameter (ϕ) in equation (2.2) did not greatly affect the results, even over the limited data range. All quantum yields for the complexed anthracene and pyrene compounds were indistinguishable from zero. Because a large amount of perylene binds to humic and fulvic acid, a wider range in F/F_0 is observed and the quantum yield calculation is therefore more credible; observed values of ϕ for perylene also approached zero.

In order to gain insight into the fundamental, molecular-level association mechanism, the effects of aqueous chemistry on PAH partitioning into humic and fulvic acids must be understood. Changes in aqueous chemistry can affect both PAH compounds and DOM present in the system, as well as their interactions with the solvent and each other. Examples of these changes are the "salting out" of PAHs with increasing salinity and the coagulation of humic acid with decreasing pH. It would be beneficial, therefore, if we could quantify the aqueous chemistry effects separately for each PAH solute and for DOM.

An idea of how aqueous chemistry effects can be separated for DOM and PAH solutes was shown in an earlier section, in which partition coefficients were plotted first as functions of pH and then as functions of ionic strength. In Figure 11a, for example, the dependence of the partition coefficient on pH at fixed ionic strength can be attributed to changes in humic acid caused by pH variations. This change in humic acid alters the hydrophobic environment within the humic structure and thus alters the solute's "humic phase" activity coefficient. For constant pH values, increases in the ionic strength cause the partition coefficient for perylene and humic acid to

decrease (Figure 11b). The difference in K_{oc} is now attributed to variations in the solute's aqueous activity coefficient, as well as its humic phase activity coefficient.

The characterization of humic material as an organic phase was the basis of the thermodynamic treatment proposed by Chiou et al. (1983). They postulated that humic material would be a less efficient organic phase than nonpolar solvents, and thus used Flory-Huggins theory to estimate solute activity in the humic phase, much like Freeman and Cheung (1981) had done earlier to describe hydrophobic sorption to natural sediments. The model of Chiou et al. (1983) was extended by Chin and Weber (1989) to account for the strong and specific interactions of humic material with both water and the hydrophobic solutes. Their modification included orientation and inductive force components of van der Waals forces in the calculation of the Flory-Huggins interaction parameter. The concepts of the Flory-Huggins model were used here in an attempt to quantify the polarity of the organic environment of humic and fulvic acid.

At equilibrium, a solute partitioned between two (or more) phases has an equal chemical potential in each phase. With the choice of pure liquid solute as the standard state, partitioning of an HOC between a humic phase and water can be quantified:

$$K_{oc} = \frac{C_p}{C_w} = \frac{\gamma_i^w V_w}{\gamma_i^p V_p \rho_p f_{oc}} \qquad (2.4)$$

where C_p is the amount of solute bound per unit mass of carbon of humic material,

C_w is the "free" solute concentration in the aqueous phase, γ_i^w and γ_i^p are the activity coefficients of the solute in the aqueous and humic phase, respectively, and V_w and V_p are the respective molar volumes of water and humic material. The density of the humic material, ρ_p, is included so that K_{oc} is ultimately expressed in the conventional units of volume per unit mass carbon.

For dilute concentrations of solute in the humic phase, the activity coefficient can be estimated by the Flory-Huggins equation (Chiou et al., 1983):

$$\ln(\gamma_i^p) = \ln(V_i) - \ln(V_p) + 1 - V_i/V_p + \chi \qquad (2.5)$$

where V_i is the molar volume of the solute and χ is the Flory-Huggins interaction parameter. Combining equations (2.4) and (2.5) gives an expression similar to that obtained by Chin and Weber (1989):

$$\log K_{oc} = \log \gamma_i^w + \log \frac{V_w}{V_i} - \log \rho_p - \log f_{oc} - \frac{1 + \chi - V_i/V_p}{2.303} \qquad (2.6)$$

Because the molar volumes of Suwannee River humic and fulvic acid are relatively small compared to polymers, the ratio of solute and humic molar volumes is included in equation (2.6).

The value χ is a dimensionless interaction parameter reflecting the intermolecular forces between the molecules in a polymer-liquid system and may be obtained experimentally by measuring the activity of the solvent in the mixture (Barton, 1983). χ is considered a Gibbs free energy parameter and thus can be

divided into entropy and enthalpy components:

$$\chi = \chi_s + \chi_h \tag{2.7}$$

The entropy term, χ_s, is determined empirically, while the enthalpy term, χ_h is frequently estimated from the Hildebrand-Scatchard equation (Barton, 1983). χ_s may vary from 0 (molecules of similar size) to 0.5 (molecules dissimilar in size). Chin and Weber (1989) selected $\chi_s = 0.34$ as the entropic value based on values for polar polymers, and also performed sensitivity analysis on the model for a range of χ_s values from 0.1 to 0.5. They found that the model was relatively insensitive to variations in χ_s over this range, presumably because of the relatively large heat of mixing for the hydrophobic organic solute and polymer.

The enthalpic component of the interaction parameter can be calculated from the Scatchard-Hildebrand equation:

$$\chi_h = (V_i / RT) A_{12} \tag{2.8}$$

where A_{12} is the exchange energy density or interchange cohesive pressure (Barton, 1983). Chiou et al. (1983) and Curtis et al. (1986) used regular solution theory and the geometric mean rule for dispersion interactions to estimate:

$$A_{12} = (\delta_i - \delta_p)^2 \tag{2.9}$$

where δ_i and δ_p are the solubility parameters of the solute and polymer, respectively.

This treatment assumes that molecular interactions between the solute and polymer are weak and dispersive, as for two nonpolar liquids. A higher value of δ_p indicates a more polar polymer. Based on the partitioning of four hydrophobic organic compounds, Chiou et al. (1983) determined an average value of 13 for the total solubility parameter of soil humic material. Curtis et al. (1986) made predictions of K_{oc} values for δ_p equal to 10.3 and 11.5. The value of 10.3 corresponded to an inferred δ_p obtained from solvent extraction studies, while 11.5 was the approximate average of this value and the value obtained by Chiou et al. (1983).

An alternative approach was used by Chin and Weber (1989). They pointed out that many naturally occurring polymers present in aquatic systems are polar, and thus interact appreciably with water through hydrogen bonding. A nonpolar solute would be expected to interact with humic substances through both dispersion forces and induction forces. They used a modified regular solution expression to describe the interchange cohesive pressure:

$$A_{12} = (\delta_i - \lambda_p)^2 + \tau_p^2 - 2\psi \qquad (2.10)$$

where λ_p and τ_p are the respective nonpolar (dispersion) and polar (orientation) cohesion parameter components of the total polymer solubility parameter. ψ is a parameter which accounts for induction interactions between the solute and polymer and has been found to be proportional to τ_p^2 (Barton, 1983). This approach recognizes the importance of all three components of the van der Waals attraction forces, and not only the dispersion forces incorporated in regular solution theory.

Unfortunately, because humic substances are complex, heterogeneous mixtures, polar and nonpolar solubility parameters can not be determined by conventional means. Chin and Weber (1989) hypothesized that the physicochemical properties of "surrogate" compounds could be used to characterize the properties of humic material, and that these properties could then be substituted into the modified Flory-Huggins model [i.e., equation (2.10)] to estimate K_{oc} values. They observed that predictions using methyl salicylate as the surrogate compound agreed well with experimental values for the binding of 14 compounds to commercial humic acids. Predictions based on the physicochemical properties of lignin and polymaleic acid consistently overestimated and underestimated, respectively, the partition coefficients.

In order to apply equation (2.6) to the observed partition coefficients, the aqueous activity coefficients for the organic solutes must be known. Activity coefficients are generally calculated from aqueous solubility data:

$$\log \gamma_i^w = \frac{-\Delta H_f}{2.303RT}\left(\frac{T_m - T}{T_m}\right) - \log(SV_w) \qquad (2.11)$$

where ΔH_f is the latent heat of fusion, R is the gas constant (1.98 cal/mol-deg), T_m is the melting point of the solute, T is 296° K, S is the solute molar saturation concentration and V_w is the molar volume of water. The first term in equation (2.11) is an expression necessary to account for the energy "cost" of melting a solid solute. If accurate heats of fusion are not available, entropies of fusion ($\Delta H_f/T_m$) have been shown to be approximately 13.5 cal/mol for many simple

aromatic compounds (Chiou et al., 1982).

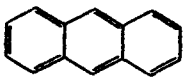
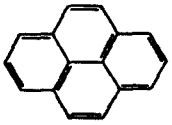
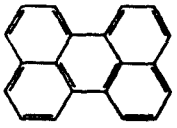
The solubilities of HOC in salt solutions are dependent on the concentration and types of electrolytes present in solution. This dependence, the magnitude of the salting-out effect, is well represented by the empirical Setschenow equation (McDevit and Long, 1952; May, 1980):

$$\log \frac{S_0}{S_s} = K_s C_s \qquad (2.12)$$

where S_0 and S_s are the concentrations of solute in water and salt solution, respectively, C_s is the molar salt concentration and K_s is the Setschenow constant. The theory developed by McDevit and Long (1952) for the salting out of HOC predicts an increase in K_s with increasing liquid molar volume of solutes (e.g., Table VI). This is because electrolyte salts increase the density of water; the closer packing of water molecules around ions is a process known as electrostriction. This contraction in total volume can be interpreted as a compression of the solvent, which makes it more difficult to insert the volume of a neutral solute. In effect, the increase in internal pressure resulting from ion-solvent interactions "squeezes out" neutral molecules.

Using the Setschenow constants in Table VII, solubilities of the PAH solutes were calculated for the various salt solutions using equation (2.12). These values were then utilized to calculate the activity coefficients with equation (2.11), using average melting point temperatures from Table II and the heats of fusion listed in Table VII

Table VI. Molecular and Molar Properties of Polycyclic Aromatic Hydrocarbons (PAHs)

	Anthracene	Pyrene	Perylene
Structure			
Carbon Number	14	16	20
Molecular Length [a] (Å)	10.5	9.5	10.5 [b]
Total Surface Area [c] ($Å^2$)	202.2	213.0	251.5
Liquid Density [d] (g/cm^3)	1.112	1.179	1.249 [e]
Molar Volume [d] (mL)	160.2 [f]	171.5 [f]	202 [g]

[a] Klevins, 1950.

[b] Estimate based on major-axis length.

[c] Yalkowsky and Valvani, 1979.

[d] Davis and Gottlieb, 1962.

[e] Calculated from molar volume.

[f] Calculated from liquid density.

[g] Estimated from correlation with solid density.

Table VII. Thermodynamic Properties Needed to Calculate PAH Solubilities and Activity Coefficients.

	Anthracene	Pyrene	Perylene
ΔH_f (kcal/mol)	6.89 [a]	4.20 [a]	7.59 [b]
ΔS_f (cal/mol-deg) [c]	14.1	9.9	13.77
K_s (M^{-1})	0.238 [d]	0.286 [d]	0.354 [e]
S (nM) [f]			
Distilled Water	409.6	667.5	1.585
0.001 M NaCl	409.3	667.0	1.584
0.01 M NaCl	407.3	663.1	1.572
0.1 M NaCl	387.7	624.9	1.461
γ_i^w [g]	($x10^{-6}$)	($x10^{-6}$)	($x10^{-7}$)
Distilled Water	1.306	9.646	8.721
0.001 M NaCl	1.307	9.653	8.727
0.01 M NaCl	1.313	9.710	8.793
0.1 M NaCl	1.380	10.303	9.461

[a] Chiou et al., 1982.

[b] Weast, 1986.

[c] Calculated from enthalpy of fusion and melting point temperature.

[d] May, 1980.

[e] Predicted value from correlation of Setschenow constant with molar volume (McDevit and Long, 1952) using data from May, 1980.

[f] Distilled water data from MacKay and Shiu, 1977.
Other data calculated with equation (2.12)

[g] Calculated with equation (2.11).

for each PAH. The entropies of fusion were also calculated to compare with the widely accepted value of 13.5 eu. In the case of pyrene, a big discrepancy exists for the actual and predicted value.

Values for χ were determined with equation (2.6) and the appropriate data from Tables III through VII. In general, for a particular PAH the value of χ increased as K_{oc} decreased (Tables VIII and IX). Assuming an entropic interaction value χ_s = 0.34 (Chin and Weber, 1989), enthalpic interaction components were calculated. For all aqueous chemistry conditions, the nonideal heats of mixing contributed a significant fraction to the total Flory-Huggins parameter.

Using equations (2.8) and (2.9), total solubility parameters were calculated for humic and fulvic acid and are listed in Tables VIII and IX, respectively. Although the modified Flory-Huggins model developed by Chin and Weber (1989) may have been a better characterization of the organic environment of humic substances, it was not possible to extract polar and nonpolar cohesion parameter components from the experimental data of this study. Also, the more complex model may not be warranted, in considering the number of assumptions needed to obtain equations (2.5) through (2.9) (Curtis et al., 1986).

The calculated values for δ_p were observed to range from 11.6 to 14.1 $(cal/mL)^{1/2}$ and were dependent on the aqueous chemistry of the system and the type of humic material used. These values fall into the general range observed by the researchers mentioned above. The solubility parameter appears to qualitatively describe the polarity of the humic phase as observed from the trends in Tables VIII

Table VIII. Calculated Flory-Huggins Parameters for Humic Acid.[a,b,c]

	Anthracene (δ = 9.9)			Pyrene (δ = 10.2)			Perylene (δ = 10.7)		
	χ	χ_h	δ_p	χ	χ_h	δ_p	χ	χ_h	δ_p
0.001 M									
pH 4	1.25	0.91	11.72	2.91	2.57	13.16	1.41	1.07	12.46
pH 7	1.14	0.80	11.62	3.21	2.87	13.33	1.58	1.24	12.60
pH 10	1.22	0.88	11.69	3.29	2.95	13.37	2.21	1.87	13.03
0.01 M									
pH 4	1.16	0.82	11.64	3.26	2.92	13.35	1.51	1.17	12.54
pH 7	1.25	0.91	11.73	3.61	3.27	13.54	1.65	1.31	12.65
pH 10	1.42	1.08	11.89	3.50	3.16	13.48	3.18	2.84	13.57
0.1 M									
pH 4	1.01	0.67	11.46	3.31	2.97	13.38	1.73	1.39	12.71
pH 7	1.61	1.27	12.06	3.78	3.44	13.62	2.37	2.03	13.13
pH 10	1.55	1.21	12.01	3.78	3.44	13.62	4.25	3.91	14.07
Ca^{2+} [d]									
pH 4	1.34	1.00	11.82	3.36	3.02	13.41	1.69	1.35	12.68
pH 7	1.25	0.91	11.72	3.46	3.12	13.46	2.51	2.17	13.21
pH 10	1.21	0.87	11.68	3.79	3.45	13.63	4.43	4.09	14.14

[a] V_w = 18.07 mL/mole, R = 1.98 cal/mol-deg, T = 296°K. [b] Anthracene solubility parameter was taken from Barton (1983). Pyrene and Perylene solubility parameters were calculated from Small's group molar attraction constants [Barton (1983)] using molar volumes listed in Table VI. Units of δ and δ_p are $(cal/mL)^{1/2}$. [c] χ_s = 0.34 [Chin and Weber (1989)]. [d] 1 mM Ca^{2+} and 0.1 M total ionic strength.

Table IX. Calculated Flory-Huggins Parameters for Fulvic Acid.[a,b,c]

	Anthracene (δ = 9.9)			Pyrene (δ = 10.2)			Perylene (δ = 10.7)		
	χ	χ_h	δ_p	χ	χ_h	δ_p	χ	χ_h	δ_p
0.001 M									
pH 4	1.63	1.29	12.07	3.76	3.42	13.61	3.58	3.24	13.77
pH 7	1.83	1.49	12.24	4.46	4.12	13.95	ND	ND	ND[e]
pH 10	1.70	1.36	12.13	4.38	4.04	13.91	ND	ND	ND
0.01 M									
pH 4	1.59	1.25	12.04	3.85	3.51	13.66	3.67	3.33	13.81
pH 7	1.91	1.57	12.30	4.71	4.37	14.06	ND	ND	ND
pH 10	1.74	1.40	12.16	4.51	4.17	13.97	ND	ND	ND
0.1 M									
pH 4	1.76	1.42	12.18	4.07	3.73	13.77	3.89	3.55	13.91
pH 7	2.03	1.69	12.39	4.69	4.35	14.05	ND	ND	ND
pH 10	1.84	1.50	12.24	4.75	4.41	14.09	ND	ND	ND
Ca^{2+} [d]									
pH 4	1.82	1.48	12.23	4.09	3.75	13.77	3.82	3.48	13.88
pH 7	1.86	1.52	12.26	4.38	4.04	13.91	ND	ND	ND
pH 10	1.74	1.40	12.16	4.13	3.79	13.79	ND	ND	ND

[a] V_w = 18.07 mL/mole, R = 1.98 cal/mol-deg, T = 296°K. [b] Anthracene solubility parameter was taken from Barton (1983). Pyrene and Perylene solubility parameters were calculated from Small's group molar attraction constants [Barton (1983)] using molar volumes listed in Table VI. Units of δ and δ_p are $(cal/mL)^{1/2}$. [c] χ_s = 0.34 [Chin and Weber (1989)]. [d] 1 mM Ca^{2+} and 0.1 M total ionic strength. [e] ND, not determined.

and IX. The values for δ_p increase with increases in pH, as would be expected for an increasingly polar material. Likewise, increases in the ionic strength would allow more charge to develop on the humic molecule, resulting in higher values for δ_p. Finally, for identical conditions, the solubility parameter for fulvic acid (Table IX) is always larger than that for humic acid (Table VIII), in agreement with the known properties of humic and fulvic acids (Table III).

The model, however, appears to be inadequate in completely describing the aqueous chemistry effects on the solute activity coefficient in the humic phase. For fixed pH, ionic strength and $[Ca^{2+}]$, the values of δ_p calculated using different PAH solutes should be similar for a given humic substance. However, as seen in Tables VIII and IX, each solute gives very different values for δ_p. These differences may be due to errors introduced in the estimation of the solute solubility parameters, or in the general failing of the simple model to accurately describe the solute-humic interaction as noted above.

Another potential source of discrepancy in model predictions of δ_p from the different PAH solutes may result from the experimental technique used to obtain the partitioning data. Because the PAH compounds used in this study are relatively insoluble in water, concentrated stock solutions of the solutes were prepared in methanol. These solutions were then spiked into the samples. Backhus and Gschwend (1990) reported that the low levels of methanol used in their study (5×10^{-3} volume fraction) were not expected to affect PAH aqueous activities significantly. However, an estimate of the effect can be made using concepts from

solvophobic theory.

The influence of an organic cosolvent on measured partition coefficients can be estimated from (Curtis et al., 1986):

$$\log\left(\frac{K_{oc}^{m}}{K_{oc}^{w}}\right) = -\left(\frac{\alpha\,\sigma^{c} f^{c}}{2.303}\right) \qquad (2.13)$$

where K_{oc}^{m} and K_{oc}^{w} are the respective partition coefficients for mixed solvent and pure water, σ^{c} is the solute-cosolvent solubility parameter, and f^{c} is the volume fraction of cosolvent. α is an empirical parameter which corrects for nonideal solute-solvent-sorbent interactions; values for α have been reported as being equal to unity for reverse-phase liquid chromatography (RPLC) (Woodburn et al., 1986), $\alpha = 0.83$ for soil sorption data (Karickhoff, 1984), and $\alpha = 0.51$ for soil and sediment data (Fu and Luthy, 1985).

The parameter σ^{c} is a function of the solvent surface tension and solute lipophilicity and can be determined by (Curtis et al., 1986):

$$\sigma^{c} = \frac{\Delta\gamma^{c}(HSA)}{kT} \qquad (2.14)$$

where $\Delta\gamma^{c}$ is the difference in surface tension of pure water and pure cosolvent, HSA is the hydrophobic surface area, k is the Boltzmann constant (1.38×10^{-23} J/K), and T is the absolute temperature (296°K). The hydrophobic surface area for PAH solutes can be assumed equal to the total surface area, and $\Delta\gamma^{c}$ for methanol has

been determined to be (2 - 2.4) x 10^{-20} J/nm^2 from RPLC systems (Woodburn et al., 1986). From equation (2.14), it can be seen that the cosolvent effect increases for compounds as their aqueous activity coefficients increase (because log $\gamma_i^w \propto$ TSA).

Equations (2.13) and (2.14) were used to estimate the decrease in observed partition coefficients due to the presence of methanol (3.3 x 10^{-3} volume fraction). High and low estimates were made based on the range of values for α and $\Delta\gamma^c$ reported. As shown in Table X, the estimated error in K_{oc} observed is approximately 2 to 5% and is relatively constant for the three solutes. Therefore, the cosolvent effect of methanol in the system does not appear to be the reason for the discrepancy in the Flory-Huggins model predictions for δ_p using different PAH solutes.

The inability of the Flory-Huggins model to characterize the hydrophobic environment of the humic substances used in this study probably results because the assumptions utilized in deriving the model do not properly portray Suwannee River humic material. The Flory-Huggins model is based on the concept that humic material forms "microscopic organic environments" similar to micelles into which hydrophobic solutes can dissolve. The formation of a substantial humic (i.e., organic) phase would probably require high-molecular weight humin-kerogen structures such as those originally proposed by Freeman and Cheung (1981) to describe natural organic material in sediments. The idea that the relatively low molecular weight humic substances used here can form organic phases appears to be erroneous.

Table X. Estimated Cosolvent Effect with PAH/Methanol Probe.[a]

	Anthracene	Pyrene	Perylene
Total Surface Area (nm^2)	2.02	2.13	2.52
$\sigma^{c\ b}$	9.9 - 11.9	10.4 - 12.5	12.4 - 14.9
Decrease in K_{oc} [c] from cosolvent	1.7 - 3.8%	1.7 - 4.1%	2.1 - 4.8%

[a] $f^c = 3.3 \times 10^{-3}$, $k = 1.38 \times 10^{-23}$ J/K, T = 296°K.

[b] $\Delta\gamma^c \approx (2 - 2.4) \times 10^{-20}$ J/nm^2 for methanol [Woodburn et al. (1986)].

[c] Low estimate for $\alpha = 0.51$, $\Delta\gamma^c = 2 \times 10^{-20}$ J/nm^2.
High estimate for $\alpha = 1$, $\Delta\gamma^c = 2.4 \times 10^{-20}$ J/nm^2.

In fact, even the depiction of Suwannee River humic material as a polyelectrolyte is not correct (Aiken et al., 1989).

The molecular-level picture of HOC-DOM associations proposed by Schnitzer and Khan (1972) appears to better describe the binding reactions observed in this study. They viewed humic material as having an open structure which allowed for a considerable number of voids of varying dimensions. The structural arrangement was expected to be sensitive to changes in pH, salt concentration and valence of cations. Schnitzer and Khan (1972) hypothesized that the voids could trap organic molecules, provided the compounds had the proper molecular sizes to fit into the holes and if the environment in the voids was conducive to association with the organic compounds. These voids, or hydrophobic cavities, would thus be sites where van der Waals bonding forces between organic molecules and DOM would occur as part of the overall hydrophobic interaction.

The effects of aqueous chemistry on the PAH binding by humic substances observed in the previous section can be easily explained using the concepts proposed by Schnitzer and Khan (1972). As noted earlier, variations in solution chemistry cause changes in the aqueous activity coefficients of HOC, as well as changes in the conformation and polarity of DOM. Although the aqueous activity coefficient of an HOC is the most important parameter overall for determining order-of-magnitude effects, it is not as sensitive to changes in solution chemistry as are the conformation and polarity of dissolved humic materials, which subsequently affect the hydrophobic environment of DOM and its ability to bind nonpolar organic molecules.

At constant ionic strength, for example, increases in pH progressively deprotonate DOM molecules but have little effect on the aqueous activity coefficient of nonpolar organic molecules (i.e., $\gamma_i^w \approx$ constant). Deprotonation increases the polarity of DOM and decreases its hydrophobicity and ability to bind HOC. At fixed pH values, increases in electrolyte concentrations tend to "salt out" HOC molecules (i.e., γ_i^w increases) but also compress DOM molecules by electrostriction (Leenheer et al., 1989). This compression decreases the size of the voids in dissolved humic substances into which HOC can partition. Because DOM is affected more than the solute's activity coefficient by the increase in electrolyte, the amount of HOC bound by humic material generally decreases.

The one exception to the trends described above was observed for the anthracene-humic acid complex. In NaCl solutions at pH 4, an increase in the ionic strength resulted in increased anthracene binding (Figure 4b). This observation is interesting because anthracene was the smallest PAH examined (TSA = 202.2 Å^2, Table VI) while humic acid was the larger DOM investigated; it seems probable that the singular behavior of anthracene under these conditions is an indication of the size of voids in the humic acid molecule.

Trends similar to those observed in this study have been reported previously by other researchers, but not in the context of Schnitzer and Khan's (1972) proposed model for HOC-DOM interactions. Karickhoff (1984) reported that studies utilizing large HOC (i.e., 5-ring or larger) found dramatic reductions, as much as an order of magnitude, in K_{oc} for particular soils/sediments. Studies utilizing smaller molecules

(1-4 rings) showed less than a factor of two variability in K_{oc} for the same sediments/soils. Karickhoff (1984) suggested these observations resulted because sorbent availability depended on sorbate size. The inability of the solute to gain access to the sorbent thus resulted in a steric inhibition of sorption.

McCarthy et al. (1989) investigated the association of benzo[a]pyrene (BaP) with 11 different DOM and correlated the values of K_{oc} with the structural and chemical properties of the organic matter. They observed that there was a good correlation between the size and hydrophobic-acid content of the DOM from different sources and the K_{oc} for binding BaP. The affinity of DOM for binding BaP appeared to be related not only to the presence of sufficient hydrophobic moiety to promote partitioning, but also to the presence of acidic functional groups. McCarthy et al. (1989) hypothesized that the acidic functional groups acted to open the structure of the DOM and that this more open structure contributed to binding of the HOC by making hydrophobic cavities within the DOM structure more accessible to the solute.

Gauthier et al. (1987) investigated the binding of pyrene by 14 different humic and fulvic acids and observed that the magnitude of the K_{oc} values correlated strongly with three independent measures of the degree of aromaticity in the humic material. They postulated that the binding mechanism was dominated by van der Waals interactions, and that the increased affinity resulted because aromatic bonds in DOM would increase the polarizability of the material, thereby increasing the strength of the van der Waals attraction forces between pyrene and DOM. Gauthier et al. (1987)

cautioned, however, that although the degree of DOM aromaticity appeared to be important for binding PAHs, the degree of aliphatic character of DOM may be more important for binding nonplanar, saturated hydrocarbon solutes.

The ideas proposed by Schnitzer and Khan (1972) are remarkably similar to current theories and concepts in the relatively new field of molecular recognition (e.g., Shepodd et al., 1988; Petti et al., 1988). This subdiscipline of modern chemistry is concerned with studying "host-guest" interactions in aqueous and organic media. A major focus of the work in this field is the design and synthesis of water-soluble macrocycles with well-defined hydrophobic binding sites which are able to bind a variety of molecular guests of varying size, shape and polarity. These hosts have been shown to tightly bind highly-insoluble guests such as anthracene and pyrene. Major binding forces which have been identified in molecular recognition studies in aqueous media are hydrophobic interactions, donor/acceptor π-stacking interactions and ion-dipole attractions (Shepodd et al., 1988).

(C) Kinetics of Partitioning. As reported previously, the binding of PAH compounds by humic and fulvic acid was observed to be very fast. For anthracene and pyrene, the binding appeared to be complete within 20 seconds for many samples, and never took longer than 3 minutes. Because of the competing reactions for perylene (binding by DOM and adsorption to walls), the kinetics of perylene partitioning were observed indirectly. However, the binding of perylene by humic and fulvic acid appeared complete within 3 minutes.

The above results agree with previous studies of the kinetics of PAH binding by DOM. Gauthier et al. (1986) found that equilibration of PAH solutions (anthracene, phenanthrene, pyrene) after adding DOM was very rapid, requiring less than 1 minute. McCarthy and Jiminez (1985) observed that the rate of binding of benzo[a]pyrene by Aldrich humic acid was also rapid. An apparent equilibrium was obtained within 5 to 10 minutes after the addition of DOM. Backhus and Gschwend (1990) found that partitioning of perylene to Aldrich humic acid, bovine serum albumin (BSA), and unaltered groundwater samples containing DOM was complete within 3 minutes. The groundwater samples were believed to contain organic colloids and/or inorganic colloids with organic coatings.

Using a gas purging technique, however, Hassett and Milicic (1985) observed a much slower binding rate for tetrachlorobiphenyl (TCB) and Aldrich humic acid. They reported an average binding rate constant, which was dependent on the DOM concentration, of 1.7×10^{-4} $(mg\ C/L)^{-1}min^{-1}$. For 1 ppm C, the half-life would therefore be approximately 3 days. Haas and Kaplan (1985) used a closed loop recirculating gas method to determine the binding of toluene to Aldrich humic acid. They observed that equilibrium was attained after 8 hours of gas circulation. The results from these two studies, however, are believed to be seriously flawed. The relatively long times reported seem to be artifacts of the methods used, and most likely are the times required for equilibration of experimental apparatus. Hassett and Milicic's (1985) rate constants varied systematically with gas flow rates, as well as DOM concentrations, indicating that desorption of TCB from the apparatus was

interfering significantly in their system. It is difficult to analyze Haas and Kaplan's (1985) results from the limited description of their method. However, interferences from adsorption to apparatus and/or gas-liquid exchange rates are plausible. Finally, it may be possible that the use of Teflon created artifacts in both of the studies, because Teflon is permeable to volatile substances and can absorb low molecular weight organic compounds (Ball and Roberts, 1991a).

The kinetic results obtained in this study for the partitioning of hydrophobic organic compounds into DOM contrast with those using sediments and soils as sorbents. The times required to attain sorption equilibria in the latter systems have been reported to be from hours to days, but in reality may proceed indefinitely (Karickhoff, 1984). Karickhoff (1980) has proposed that there are two kinetically distinct components to sorption reactions onto sediments, a rapid component requiring at most a few minutes to reach equilibrium and a much slower component requiring up to weeks to equilibrate. The latter component is thought to reflect an intraparticle process whereby a compound is slowly incorporated into either particle aggregates or sorbent components (Karickhoff, 1984). The incorporation into the sorbent matrix is contemplated as being responsible for the relative resistance to extraction observed for some sorbed chemicals. This behavior is exemplified by the increasingly difficult recovery of sorbed compounds as the incubation time increases; observations of the phenomena have been described as an "aging" of the sorbed compound (Voice and Weber, 1983).

The differences observed between binding of hydrophobic organic compounds

by DOM and by soils and sediments may be attributed to the presence of mineral surfaces and/or high molecular weight organic material in soils and sediments. Ball and Roberts (1991a,b) found that sorption of organic chemicals onto sandy aquifer material required contact times on the order of tens to hundreds of days to reach equilibrium, with physical adsorption to mineral surfaces the most significant contribution to the total amount sorbed. The rate of sorptive uptake was modeled successfully with an intraparticle diffusion model incorporating retarded transport in the constricted internal pores. This interpretation concurred with the observation that extremely long extraction times (230 days) were required to recover the sorbed compounds from unaltered material, while a shorter time (30 days) was sufficient for extracting pulverized material.

Organic material present in sediments and soils consists of relatively insoluble, high molecular weight macromolecules compared to organic material present in natural waters (i.e., DOM). While molecular weights of aquatic humic acids are generally in the range from 1000 to 10,000, those for soil humic acids have been reported to be from 2600 to more than 1 million (Kile and Chiou, 1989), and the largest fraction of humic substances in lake sediments falls into the molecular weight ranges 5000-100,000 and > 100,000 (Ishiwatari, 1985). Therefore, the organic material in sediments and soils may indeed be composed of the humin-kerogen structures proposed by Freeman and Cheung (1981). Diffusion of organic solutes into such a three-dimensional network and their subsequent incorporation into a gel would agree with the observed results for partitioning into sediment and soil organic matter.

Fluorescence Quenching. (A) Mechanism and Methods. As mentioned earlier, the static fluorescence quenching technique for determining partition coefficients is relatively rapid and simple to use, but the mechanisms of energy transfer have not previously been discussed. A lack of understanding of these mechanisms has resulted in studies which mistakenly claim to have used fluorescence quenching to determine adsorption constants of PAH compounds to mineral surfaces (Shimizu and Liljestrand, 1991; Liljestrand and Shimizu, 1991).

When PAH compounds are associated with a potential quencher, the last two requirements of Förster theory are satisfied, and the only remaining criteria are that the donor and acceptor have a substantial spectral overlap and that the extinction coefficient of the acceptor integrated over the absorption band is large. These last two conditions are obviously not satisfied for mineral surfaces. This prediction from Förster theory is verified by observations that inorganic materials are commonly used as substrates for studying the photochemistry of adsorbed organic molecules and that fluorescent molecules have been used to probe the solid-liquid interfacial region of inorganic colloids (Kalyanasundaram, 1987).

Backhus and Gschwend (1990) observed exponential decreases in solution fluorescence intensities as perylene was adsorbing to their glassware (syringes) during an experiment. Perylene was being lost from solution to syringe walls before the transfer of samples to fluorescence cells for measurements. They modeled the loss of perylene from solution with a simple first-order rate expression. This study used fluorescence cells both as reaction vessels and for measuring perylene concentrations

in solution. The observed exponential decrease in fluorescence with time resulted from removal of perylene (still fluorescent) from the path of the excitation source and/or from the view of the detector. The decrease in intensity was observed because of the particular geometry of the spectrofluorophotometer, not because the fused silica surface was quenching perylene fluorescence.

For PAHs which do not sorb to experimental glassware, the fluorescence quenching method developed by Gauthier et al. (1986) is a simple, rapid and elegant technique. The data can be analyzed equally well with either equation (2.1) or (2.2). Its major benefits are that it requires no separation of bound pollutant from free pollutant and it does not require the initial concentration of pollutant to be known. One or both of these two points have been remarked upon by other researchers who have utilized fluorescence quenching to study PAH partitioning by DOM (Traina et al.,1989; Backhus and Gschwend, 1990; Shimizu and Liljestrand, 1991). The second point, however, seems to have been thoroughly understood only by Backhus and Gschwend (1990). The initial concentration of the pollutant does not need to be determined only if the PAH solution is titrated with DOM. This is because the total PAH concentration does not change (after dilution corrections). If PAH molecules are added to different vessels, however, at least relative PAH concentrations must be known to account for possible differences in the total PAH concentration in each vessel.

(B) Quenching Efficiency. As shown in Table V, the quantum yields of anthracene, pyrene, and perylene all approached zero when they were associated with

humic or fulvic acid. For anthracene and pyrene, the values for K_{oc} obtained using equations (2.1) and (2.2) were similar, suggesting that ϕ values obtained were credible despite the relatively low decrease in fluorescence observed.

Few published results are available for the quantum yields of PAH-DOM complexes. Backhus and Gschwend (1990) found that Aldrich humic acid fully quenched the fluorescence of perylene associated with it ($\phi \approx 0$), while bovine serum albumin (BSA) quenched only 42 percent of the associated perylene fluorescence ($\phi = 0.58$). The observations of Gauthier et al. (1986) suggest that values of zero for ϕ are found for a wide variety of humic and fulvic acids. However, as noted by Backhus and Gschwend (1990), caution must be used in interpreting Stern-Volmer plots. Previously, the appearance of linear Stern-Volmer plots has been used to argue that binding of the probe by organic matter results in complete quenching of probe fluorescence. However, as shown in Figure 12, the deviations from linearity may be subtle and easily overlooked, particularly if there is significant scatter in the data or if the ratio F_0/F is relatively low (<1.2). Unless quenching efficiencies are determined, observed values for K_{oc} should be considered lower limit estimates for the "true" K_{oc} values (Backhus and Gschwend, 1990).

The quantum yield of PAH-DOM complexes cannot be determined directly for natural waters with a given quantity of DOM of unknown composition unless the samples can be diluted or concentrated to provide a range of DOM concentrations for analysis with equation (2.2). Unfortunately, because intermolecular interactions between components of DOM are dependent on DOM concentration

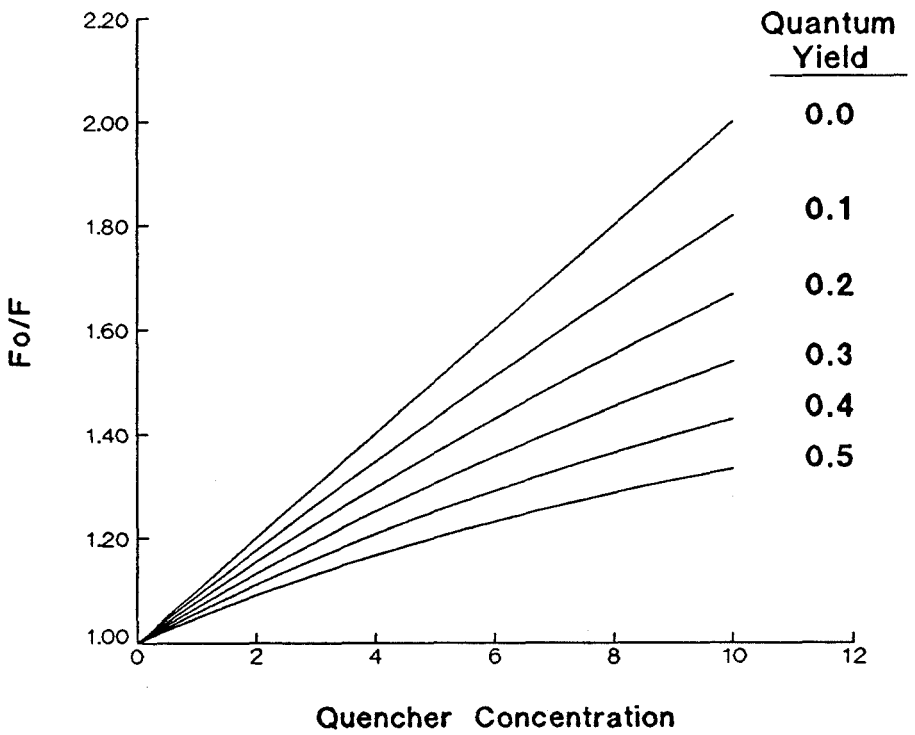


Figure 12. The effect of quenching efficiency on the linearity of Stern-Volmer plots.

(Leenheer et al., 1989), it is possible that the DOM's ability to bind organic pollutants may be altered with dilution or concentration.

Backhus and Gschwend (1990) examined groundwater samples from three different monitoring wells in order to determine the in situ organic material's ability to bind perylene. They spiked both whole and ultrafiltered (500 MWCO) samples with the PAH probe, and found that the perylene fluorescence in the ultrafiltered water, which contained between 0.7 and 1.8 mg of C/L residual organic material, never differed from that measured in blank water samples. They interpreted this observation as an indication that the ultrafilterable organic matter did not bind perylene. This interpretation is consistent with the observations of Chiou et al. (1986, 1987), who found that relatively large molecular weight (size) DOM material was necessary in order to bind a hydrophobic solute. However, the possibility that the residual organic material binds perylene, but does not quench any of its fluorescence (i.e., $\phi = 1$), cannot be excluded on the basis of Backhus and Gschwend's (1990) data. For example, although the fulvic acid used in the present study had only a slightly higher molecular weight (800 daltons) than the molecular weight cutoff ultrafiltration membrane used by Backhus and Gschwend (1990), it was able to bind perylene substantially (Table V).

From the conditions specified by Förster theory, static fluorescence quenching of a PAH compound by DOM will be most favored when there is a large spectral overlap combined with a large DOM extinction coefficient. Förster theory cannot predict, however, whether the fluorescence will be totally or only partially quenched.

As noted by Backhus and Gschwend (1990), the ability to predict efficiencies would be very useful in the application of a fluorescence quenching method, especially for natural samples. They have proposed that a correlation may exist between the degree of spectral overlap and ϕ.

Figure (13a) shows the fluorescence emission spectrum of anthracene and the absorbance spectra of humic and fulvic acid. The absorbance spectra of both humic and fulvic acid overlap the emission spectrum of anthracene to a significant extent, and extinction coefficients of humic acid are larger than those of fulvic acid for the spectral overlap wavelengths. It would be expected, therefore, that the fluorescence intensity of anthracene bound by either humic or fulvic acid would decrease relative to freely dissolved anthracene. Unfortunately, efficiency of static quenching with respect to the degree of spectral overlap and magnitude of extinction coefficients is at best a qualitative idea. It is not yet possible to predict whether the fluorescence of bound anthracene will be totally or only partially quenched. It can only be estimated that the quantum yield of anthracene bound by humic acid will be less than or equal to that of the anthracene-fulvic acid complex. Likewise, upon comparing the emission spectra of the three PAH compounds (Figure 13), an estimate of the relative quantum yields for the bound PAH's would be ϕ(anthracene) $\leq$ ϕ(pyrene) $\leq$ ϕ(perylene).

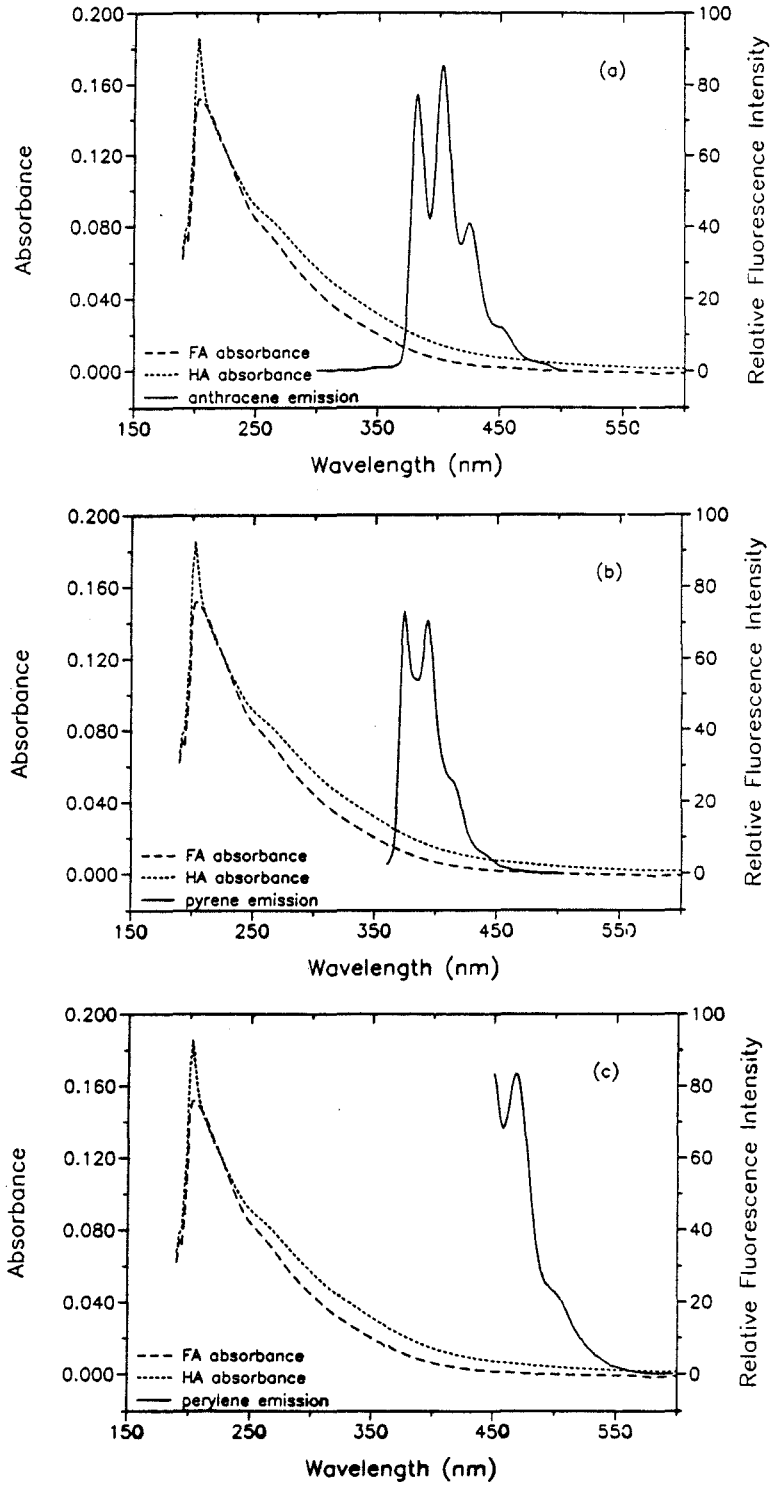


Figure 13. Relative fluorescence emission spectra of PAH compounds in aqueous solution and absorbance spectra of humic substances. Humic acid and fulvic acid concentrations are 3.35 mg/L and 3.95 mg/L, respectively. a) Anthracene. b) Pyrene. c) Perylene.

SUMMARY AND CONCLUSIONS

This study investigated the effects of aqueous chemistry on the ability of dissolved Suwannee River humic substances to bind anthracene, pyrene and perylene. These nonpolar, nonionogenic compounds were selected as model organic pollutants in order to eliminate or minimize adsorption mechanisms other than the hydrophobic interaction. By varying the pH, ionic strength and composition of the background electrolyte, the influence of solution chemistry on carbon-normalized partition coefficients was observed.

A goal of this study was to elucidate the mechanisms by which nonpolar HOC associate with DOM. Current macroscopic concepts of hydrophobic partitioning were reviewed, and two molecular-level descriptions of the association between nonpolar organic compounds and humic substances were presented. Macroscopically, the association of HOC with DOM is postulated to result from hydrophobic interactions, a combination of van der Waals attraction forces and the increased entropy which results upon breakdown of the coordination shell of water molecules surrounding the solute. Although the molecular-level models differ, they both require that hydrophobic environments be present in the humic material. A major difference between the two models is the description of the humic structure and its associated hydrophobic environment. The model proposed by Freeman and Cheung (1981) views humic material as highly-branched polymer chains which form complex three-dimensional networks. The association of nonpolar HOC with humic material would thus be a dissolution of the solute into an organic-like phase. The model proposed

by Schnitzer and Khan (1972) pictures humic material as an open structure with voids into which organic molecules would be trapped and held by van der Waals interactions.

Fluorescence quenching methods were utilized to quantify the amount of PAH solute bound by humic material. Simple concepts of energy transfer were presented in order to elucidate the mechanisms by which the fluorescence of organic molecules is statically quenched. For PAH compounds which do not sorb appreciably to experimental glassware, the fluorescence quenching method developed by Gauthier et al. (1986) is a simple, rapid and elegant technique. For very hydrophobic PAH compounds which sorb to inorganic surfaces, the fluorescence quenching method (kinetic approach) developed by Backhus and Gschwend (1990) is an equally elegant (albeit more cumbersome) technique. The major benefits of fluorescence quenching methods are that (1) no separation of DOM from water is required, (2) exact pollutant concentrations need not be known, and (3) fluorescence is an inherently sensitive technique which can detect very low pollutant concentrations.

The binding of PAH solutes by humic and fulvic acid was observed to be a relatively fast reaction. For anthracene and pyrene, the binding appeared to be complete within 20 seconds for many samples and never exceeded 3 minutes. The binding of perylene also appeared to be equilibrated within 3 minutes. For the PAH compounds associated with DOM, fluorescence appeared to be fully quenched by Suwannee River humic and fulvic acid, as evidenced by quantum yield values which approached zero for all complexes.

Association of PAH compounds with dissolved humic and fulvic acid was influenced by solution chemistry for the samples analyzed here. In NaCl solutions, the amount of a PAH bound by a particular DOM generally decreased with increasing pH (constant ionic strength), and also generally decreased with increasing ionic strength (fixed pH). The presence of Ca^{2+} had mixed results; at pH 4 it typically had little effect or else decreased the amount of PAH bound relative to a NaCl solution. At pH 7 and 10, however, the presence of Ca^{2+} generally increased the amount of bound PAH relative to NaCl solutions. The one major deviation from these observed trends was the binding of anthracene by humic acid at pH 4; for this particular complex, the PAH-DOM association was observed to increase with increasing NaCl concentrations.

Results obtained from the binding studies were analyzed with a thermodynamic treatment based on the model developed by Chiou et al. (1983) in an attempt to understand the molecular-level mechanisms of PAH-DOM interactions. Based on concepts similar to the molecular-level representation of Freeman and Cheung (1981), the model utilizes Flory-Huggins theory to estimate solute activity coefficients in the humic phase. With this model, it is possible to quantify the polarity of the organic environment of humic and fulvic acid with varying aqueous chemistry conditions.

Although the Flory-Huggins model was able to qualitatively describe the polarity of the humic phase for the PAH compounds, each solute gave very different estimates of the DOM solubility parameter for identical solution conditions. The

inability of the model to characterize the hydrophobic environment of humic substances results because the assumptions utilized in the derivation do not properly depict Suwannee River humic material. The Flory-Huggins model is based on the idea that humic material forms "microscopic organic environments," similar to micelles, into which hydrophobic solutes can dissolve; the relatively low molecular weight humic substances from the Suwannee River are apparently too small to form such an organic phase.

The molecular-level representation of HOC-DOM associations proposed by Schnitzer and Khan (1972) appears to better describe the trends of the binding reactions observed here. Their picture of humic material as an open structure with hydrophobic cavities appears plausible. The dimensions and hydrophobicity of the voids in these structures would be sensitive to variations in pH, salt concentration and valence of cations. Because the properties of the voids change with varying solution chemistry, a subsequent change in the ability to bind HOC would occur, much like the trends observed in this study.

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Chapter 3

THE ADSORPTION OF AQUATIC HUMIC SUBSTANCES ON COLLOIDAL-SIZED ALUMINUM OXIDE PARTICLES: A STUDY OF THE FORMATION OF ORGANIC COATINGS

ABSTRACT

The adsorption of Suwannee River humic substances on colloidal-sized aluminum oxide particles was examined. The amount of humic and fulvic acid adsorbed decreased with increasing pH for all solutions of constant ionic strength. In NaCl solutions at fixed pH values, the adsorption of humic material increased with increasing ionic strength. The presence of Ca^{2+} enhanced the adsorption of humic acid but had little effect on fulvic acid adsorption. For identical solution conditions, the amount of humic acid adsorbed to alumina was always greater than that of fulvic acid. Adsorption densities for both humic and fulvic acid showed good agreement with Langmuir isotherms, and interpretations of adsorption processes were made from the Langmuir parameters. For fulvic acid, ligand exchange was the most important adsorption mechanism for all conditions analyzed. Ligand exchange was also a major adsorption mechanism for humic acid; however, hydrophobic bonding and bridging mechanisms contributed to adsorption as solution composition changed. Calculations of carboxyl group densities in the adsorbed layer supported the proposed adsorption mechanisms. From the adsorption data, it appears that a maximum of 3.3 COO^-/nm^2 can be bound directly as inner-sphere complexes by the alumina surface. It is postulated that the influence of aqueous chemistry on humic material adsorption mechanisms, and therefore on the types of surface complexes formed, affects the formation and nature of organic coatings on mineral surfaces.

INTRODUCTION

Solid surfaces are the sites of many important geochemical phenomena in natural aqueous systems; many chemical reactions that occur in natural waters take place at solid-solution interfaces. For example, the formation, aggregation, sedimentation and dissolution of particulate material are all controlled by processes which occur at solid-liquid interfaces.

The adsorption of natural organic material (NOM) on particle surfaces has long been recognized as an important geochemical process in soils (Stevenson, 1985; Sposito, 1984, 1989). Only relatively recently, however, has its importance been recognized in aquatic systems (Malcolm, 1985). In the environment, NOM adsorbs at particle surfaces and can dominate the properties of the solid-liquid interface. While only a fraction of the NOM in aquatic systems may be adsorbed on particle surfaces, the solid surface may be entirely covered by organic material and thus exhibit the physicochemical properties of the organic matter. In effect, the adsorbed species may be thought of as an organic "film" coating particle surfaces.

The presence of NOM at the solid-liquid interface can greatly affect geochemical reactions in aqueous systems. Recent studies have noted the potential significance of adsorbed NOM on the chemical and physical properties of colloidal particles suspended in natural waters. Tipping and Davis and their respective coworkers (Tipping, 1981; Tipping and Cooke, 1982; Davis, 1980, 1982; Davis and Gloor, 1981) all observed that oxide particles with positive electrophoretic mobility reversed their mobility in the presence of very small amounts of NOM. Other

researchers have observed increased stability for particles with adsorbed NOM (Gibbs, 1983; Ali et al., 1984; Tipping and Higgins, 1982; Tipping and Ohnstad, 1984). Liang and Morgan (1990a,b) studied the effects of Suwannee River humic substances on the stability of hematite particles. They observed a sharp initial decrease in stability (100 times) within a factor of 10 increase in organic concentration followed by an equally sharp or sharper increase in particle stability (restabilization) after the organic concentration was increased beyond the critical coagulation concentration.

The geochemistry, and ultimately the fate, of particles and particle-reactive compounds is strongly dependent on chemical reactions that occur at the solid-liquid interface of particles. These reactions can greatly affect the mobility, bioavailability, reactivity and toxicity of pollutants. Organic surface coatings modify particle-pollutant interactions which occur in the solid-liquid interface or on particle surfaces. Because stabilization of particles by NOM is a common observation, the transport and fate of NOM, particles and particle-reactive compounds in natural waters are complex, interdependent processes.

The mechanisms by which NOM adsorbs at mineral surfaces are largely dependent on solution composition parameters such as pH, ionic strength, and bivalent cation concentrations (Sposito, 1984). The different adsorption mechanisms determine the type of particle-NOM complex which forms and this, in turn, affects the reactions which take place at the solid-liquid interface. For example, NOM-enhanced weathering of minerals is thought to occur if the NOM is bound at

a mineral surface via an inner-sphere complex. In this process, ligand exchange is considered to be a first step in the dissolution of a hydroxylated mineral by NOM carboxyl groups. Subsequent steps involve the polarization of critical metal-oxygen bonds by the surface complex and ultimate detachment of the metal-ligand complex into the aqueous phase (Sposito, 1989).

The type of NOM-surface complex which exists at a solid-liquid interface is also thought to affect pollutant binding by particles. Thus, it is necessary to identify the mechanisms by which NOM adsorbs to mineral surfaces. This study investigated the adsorption of well-characterized NOM on a hydrous oxide surface. It was postulated that the conformation and polarity of NOM play important roles in its adsorption onto mineral surfaces. Because the adsorption mechanisms are affected by the aqueous chemistry of natural waters, a systematic study of the effects of pH, ionic strength and presence of bivalent cations was undertaken. The objectives of this study, therefore, were to (1) quantify the adsorption of NOM onto colloidal particles, (2) identify the principal mechanisms by which NOM adsorbs to mineral surfaces, and (3) determine how changes in solution composition can affect the relative importance of the different adsorption mechanisms.

EXPERIMENTAL

Apparatus. Organic carbon concentrations were measured with a Shimadzu Model TOC-500 total organic carbon analyzer. This instrument uses a high sensitivity catalyst to oxidize carbon compounds at 680°C and a nondispersive infrared detector to measure CO_2 produced. Because of the relatively low temperature, quantitative calculations for total carbon in a sample are based upon measured peak areas. Ultrapure air (Scott-Marin Inc., Riverside, CA) was used both as the combustion and carrier gas and was certified to contain less than 1 ppm CO_2 (v/v). Initially, dilutions of a 1000 mg/L potassium biphthalate solution prepared with 0.01 M HCl were used to calibrate the instrument (i.e., sample concentration units obtained as mg carbon per liter solution). Later, after observations of a decrease in the oxidation efficiency of the humic substances with increasing catalyst age, measurements utilized standard humic/fulvic acid solutions prepared with 0.01 M HCl to obtain a calibration curve directly (i.e., mg humic material per liter solution obtained for sample concentration).

The pH of all aqueous solutions was measured with a Radiometer Model PHM84 Research pH Meter using a Radiometer GK2401C glass combination electrode. The pH meter was calibrated with NBS buffers.

Materials. (A) General. All reagents not specifically referred to were of analytical grade or better and were used without further treatment. All aqueous stock solutions were filtered through 0.2 μm pore polycarbonate Nuclepore filters.

(B) Humic Substances. Well-characterized humic materials were obtained from the International Humic Substances Society (IHSS) and used without further

purification. Suwannee River standard humic acid and Suwannee River standard fulvic acid were isolated from the Suwannee River which drains the Okefenokee Swamp in southern Georgia. Isolation procedures and characterization of these materials have been reported (Averett et al., 1989). Chemical properties of the humic and fulvic acids are shown in Table I and some physical properties are listed in Table II.

Because the humic materials received are very hygroscopic, they were stored in a desiccator until needed. Concentrated stock solutions were prepared by dissolving weighed amounts of the humic material in deionized, distilled water (D_2H_2O). The solutions were mixed and allowed to stand in the dark for at least 24 hours. The humic stock solutions were filtered through prewashed 0.2 μm pore polycarbonate Nuclepore filters to remove possible particle contamination and were then stored in the dark at 4°C in amber borosilicate glass bottles.

Absorbance spectra and measurements (Hewlett Packard 8451A Diode Array Spectrophotometer) at the wavelength of 250 nm were taken of the humic and fulvic acid stock solutions before and after filtering to check for possible loss and/or fractionation of material. No such effects were observed.

(C) Aluminum Oxide Particles. The hydrous oxide particles used in this study were γ-Al_2O_3 (Degussa, Aluminum Oxide C). Aluminum Oxide C is produced by flame hydrolysis of anhydrous aluminum chloride and Debye-Scherrer x-ray diffraction patterns reveal that it has primarily a gamma structure with a slight delta structure. The chemical purity is >99.6% and the density is 2.9 g/cm^3. Other

Table I. Chemical Properties of IHSS Standard Suwannee River Humic Substances.

Elemental Analysis (%) [a] and Atomic Ratios [b]

(Ash-Free and Moisture-Free Basis)

	C	H	O	N	S	P	Total	Ash	O/C [b]	H/C [b]	C/N [b]
Humic Acid	54.22	4.14	39.00	1.21	0.82	0.01	99.40	3.19	0.54	0.91	52.25
Fulvic Acid	53.75	4.29	40.48	0.68	0.50	0.01	99.71	0.82	0.57	0.95	92.18

[a] Supplied by International Humic Substances Society (IHSS).

[b] Calculated from elemental analysis.

Structural Carbon Distributions [a]

(% of Total Carbon)

	Ketone-C (220-180)	Carboxyl/ Carbonyl-C (180-160)	Aromatic-C (160-105)	Aromatic/ Acetal-C (105-90)	Aliphatic -HCO (90-60)	Aliphatic -CH (60-0)	sp^2 (220-90)	sp^3 (90-0)	Aromaticity f_a [b]
Humic Acid	7	16	42	6	12	17	71	29	0.42
Fulvic Acid	6	19	28	5	15	27	58	42	0.28
group density [c] (g/mL)	1.74	1.878	1.601	1.601	1.620	0.72			

[a] Determined from liquid-state ^{13}C NMR [ppm range shown in parentheses] (Thorn, 1989).

[b] f_a = spectrum area from 160-105 ppm divided by total spectrum area.

[c] Group density contribution to calculated density (Brown and Leenheer, 1989).

Table II. Physical Properties of IHSS Standard Suwannee River Humic Substances.

	Humic Acid	Fulvic Acid
Radius of Gyration (Å) [a]		
pH 6	11.1	7.2
pH 9	11.4	7.7
M_n (daltons)	1100 [a]	800 [b]
Density (g/mL) [c]	1.508	1.427
v_{app} (mL/g)	0.6631	0.7008
V_p (mL/mole) [d]	730	560

[a] Determined by small-angle X-ray scattering (Aiken et al., 1989).

[b] Determined by vapor-pressure osmometry (Aiken et al., 1989).

[c] Calculated from structural carbon distributions (Table III).

[d] $M_n \div$ Density.

manufacturer data are listed in Table IV. Aluminum Oxide C has been used for adsorption studies by previous researchers (e.g., Kummert and Stumm, 1980; Bales and Morgan, 1985; Davies, 1985; Schultess and Sparks, 1987).

(1) Preparation of Stock Suspension. Aluminum oxide particles were washed in 0.1 M NaOH for two hours, rinsed once with D_2H_2O and washed again for 30 minutes in 0.1 M HCl. Pretreatment of γ-Al_2O_3 with only NaOH reportedly forms nordstrandite and bayerite (Furrer and Stumm, 1986). After centrifuging and discarding the supernatant, the oxide was scraped from the centrifuge bottles and resuspended with fresh solution. Tiny dark spots were observed in the oxide after centrifuging and were removed before resuspension of the material. Schultess and Sparks (1987, 1988) reported a similar observation; they hypothesized the impurity to be an unknown metal chloride. After more than 20 rinses the conductivity of the supernatant reached a plateau of 4 μS, approximately the same value as for deionized water. The conductivity was measured with a YSI 3403 pyrex conductance cell (K = 1.0 cm^{-1}) connected to a YSI Model 35 digital conductance meter . A loss of fines was noted during the rinsing procedure while decanting the supernatant after centrifuging. The washed particles were resuspended in D_2H_2O and stored as a concentrated suspension (10-11 g/L) in an acid-washed Nalgene bottle; a glass bottle was not used because of the potential for silicate contamination (Kebler et al., 1989).

(2) Size Distribution and Specific Surface Area. The size distribution of washed alumina particles was obtained using a Philips EM 430 transmission electron microscope (TEM) at 300 kV. An aliquot of the concentrated stock suspension was

repeatedly diluted with D_2H_2O and sonicated until a suspension of approximately 1 mg/L was obtained. A drop of the dilute suspension was placed onto a substrate consisting of a copper mesh covered with carbon film. After 30 seconds, the excess liquid was drawn off with a piece of filter paper. Although the quality of the micrographs was poor, the particles appeared to range in size from 14 to 50 nm, with an average particle diameter of 26 nm. This number contrasts with the manufacturer's stated average diameter of 20 nm; the deviation most likely resulted from loss of fines during washing of the material. Most of the particles appeared aggregated; however, this may have been an artifact which resulted upon drying the sample before TEM analysis.

With the assumption of spherical particles, a theoretical specific surface area can be calculated:

$$SA = \frac{1}{\rho}\left(\frac{\pi d^2}{\pi d^3/6}\right) = \frac{6}{\rho d} \qquad (3.1)$$

where ρ is the particle density (2.9 g/cm^3) and d is the average particle diameter (26 nm). The specific surface area is thus calculated to be 79.6 m^2/g.

The specific surface area of the washed aluminum oxide particles was determined experimentally utilizing a gravimetric method based on the retention of 2-ethoxyethanol (ethylene glycol monoethyl ether or EGME) (Eltantawy and Arnold, 1973). EGME is thought to cover all easily accessible surfaces with a unimolecular layer and has been widely used to determine the surface area of clay

materials. The method requires only readily available laboratory equipment and is a simple and effective technique for determining the specific surface area of small particles.

Approximately 0.2 g of washed aluminum oxide material, which had been dried for 24 hours at 110°C, was wetted with 3 mL EGME in a weighing bottle. The weighing bottle was placed in an ultrasonic bath briefly to help suspend the alumina and form a uniform slurry, and then the slurry was allowed to equilibrate in a dry atmosphere for one hour. The slurry was placed in a desiccator containing 100 g dry $CaCl_2$ and a free surface of liquid EGME (approximately 40 mL). The desiccator was evacuated with a vacuum pump at room temperature until the alumina appeared to be dry and the volume of liquid EGME had decreased approximately by half. The pump was then shut off and the sample was left in the sealed desiccator for one hour to equilibrate before dry air was admitted. The weighing bottle was then quickly weighed and the EGME adsorbed determined by difference. The process was repeated a second time using the same aluminum oxide material to assure the sample surface had been equilibrated with EGME. The amount of EGME retained did not change after the first equilibration.

The theoretical value for complete surface coverage with a unimolecular layer of EGME, assuming each molecule occupies approximately 40 $Å^2$ of surface, is 3.71×10^{-4} g/m^2. Specific surface area is calculated by determining the amount of EGME retained (g/g particles) and dividing by the theoretical value. The specific surface area for the washed alumina particles was thus determined to be 80 m^2/g.

This number is lower than that reported by the manufacturer, but agrees very well with previously reported values for Aluminum Oxide C which was subjected to similar washing procedures (Table IV). The measured specific surface area is in excellent agreement with the calculated value and indicates that the particles are relatively nonporous.

(3) Exchange Capacity and Site Density. The exchange capacity (EC) of the aluminum oxide particles was determined by a fluoride adsorption/desorption technique similar to that used by Liang (1988). Teflon beakers were used to avoid complexation and/or release of fluoride by experimental glass vessels.

An aliquot (5 mL) of concentrated alumina suspension was diluted with 15 mL of D_2H_2O and sonicated for 10 minutes to break up aggregates. This suspension was then added to 20 mL of 0.1 M NaF solution. The pH was adjusted to 3.7 by adding 5 mL of 0.1 M $HClO_4$ (V_T = 45 mL), and the suspension was allowed to equilibrate for approximately 3 hours. After the initial adsorption period, three 10 mL aliquots of the suspension were filtered through individual 50-nm pore polycarbonate Nuclepore filters utilizing a vacuum pump, and each filtrate was discarded. The particles and filters were rinsed with 5 mL dilute $HClO_4$ (pH ~ 4), and then the filters were placed into a beaker containing 50 mL D_2H_2O and 5 mL NaOH (pH = 11.4) in order to resuspend the particles and desorb the fluoride.

The solids concentration in the desorption suspension was determined indirectly. An aliquot (500 μL) of the remaining adsorption suspension was filtered through a preweighed 15-nm pore filter. The filter was dried for 24 hours at 110°C,

allowed to cool in a desiccator and weighed again; the mass of particles collected was determined by difference. The original solid concentration in the adsorption suspension was calculated, and this value was multiplied by the volume filtered (30 mL) to obtain the total mass of particles present in the desorption suspension. After a 3 hour desorption period, the suspension was drawn into a syringe and filtered using positive pressure through a prewashed 50-nm pore filter contained in a Nuclepore Swin-Lok holder. The first 1 mL of filtrate was discarded and the remainder was kept for fluoride determination.

The desorbed fluoride concentration was measured using the SPADNS colorimetric technique (Standard Methods, 1989). The method is based on the reaction between fluoride and a zirconium-dye lake. Fluoride reacts with the dye lake, dissociating a portion of it into a colorless complex anion (ZrF_6^{2-}) and the dye. As the amount of fluoride increases, the color produced (determined photometrically at 570 nm) becomes progressively lighter. Although the reaction between fluoride and zirconium ions is almost instantaneous, the samples and standards were allowed to stand overnight after addition of the dye lake before recording the absorbance in order to eliminate potential interference from Al^{3+}.

The exchange capacity, calculated as the moles of fluoride released from the particles divided by the solid mass present, was determined to be 2.24 mmoles/g. The site density, obtained by dividing the exchange capacity by the specific surface area, was calculated to be 16.9 nm^{-2}. This site density is higher than that reported by other researchers (Table IV), but is close to the values predicted from crystallographic

structure. The discrepancies in experimental site densities no doubt result from the use of different techniques to measure exchange capacities; from Table IV, it is apparent that the method used to determine exchange capacities influences the magnitude of the value obtained, with saturation techniques consistently giving the lowest values. No researcher has previously used a fluoride adsorption/desorption technique to determine exchange capacities for γ-Al_2O_3.

(4) Surface Titrations. Acid-base titrations of the aluminum oxide particles were performed to determine the surface chemical properties. The procedure was similar to the method used by Scott (1991) to determine surface acidity constants for goethite. The titrations were performed in a 100-mL double-walled reaction vessel connected to a constant temperature (25°C) water bath. The suspensions were mixed with a Teflon-coated stir bar driven by a magnetic stirrer. $N_{2\,(g)}$ was used to continually purge and keep the system free of $CO_{2\,(g)}$, because HCO_3^- and/or CO_3^{2-} has been postulated as being able to adsorb to aluminum oxide surfaces (Kebler et al., 1989). The gas was passed through a column of Ascarite II to remove any contaminant $CO_{2\,(g)}$, and was then rehydrated by passing through a column of D_2H_2O before being introduced into the reaction vessel.

Titrations were performed on aqueous suspensions consisting of a known solid concentration and varying NaCl concentrations. Solid concentrations were determined gravimetrically as described above prior to the titration; a concentration of ~2 g/L was used in order to have a surface site concentration of approximately 5 m<u>M</u>. Aliquots of the concentrated aluminum oxide suspension were diluted with D_2H_2O,

sonicated to break up aggregates and then added to electrolyte solutions in the titration vessel. After purging with $N_{2\,(g)}$ overnight, 300 μL of 0.1 N HCl was added to each suspension and the system was allowed to equilibrate for approximately 2 hours (pH ~ 4). This period of time facilitated additional removal of $CO_{2\,(g)}$, but was not long enough for the alumina to dissolve appreciably (Furrer and Stumm, 1986). The initial pH was recorded, and the suspension was titrated to pH 10 by adding 25-100 μL of 0.1 N NaOH at intervals of 5 to 15 minutes. Blank electrolyte solutions were likewise titrated in order to determine the amount of base consumed by surface reactions alone.

(5) Surface Speciation from Experimental Data. The experimental titration data were fit to several different surface chemistry models using FITEQL, an iterative non-linear least squares optimization computer program (Westall, 1982). The surface chemistry of metal oxides has been discussed in detail in the literature (Schindler and Stumm, 1987; Westall, 1986, 1987; Dzombak and Morel, 1990), as have the relative merits of different surface complexation models (Westall and Hohl, 1980; Dzombak and Morel, 1987). The zero point of charge obtained for the alumina particles was approximately pH 8.5.

Table III summarizes the surface properties of the γ-Al_2O_3 particles characterized in this study and the techniques used to obtain the values. The results obtained by other researchers for the same or similar aluminum oxide material are presented in Table IV for comparison.

The surface acidity constants determined for Aluminum Oxide C (Table III)

Table III. Surface Properties of Aluminum Oxide.

Formula		γ-Al_2O_3	
Specific Surface Area (m^2/g) (EGME Retention)		80	
Exchange Capacity (mmoles/g) (Fluoride Adsorption/Desorption)		2.24	
Site Density (nm^{-2})		16.9	
Surface Acidity Constants			
Model	Diffuse Layer	Stern Layer	
C_1 (F/m^2)	---	6.0	5.4
pK_1^s	6.8	7.7	8.2
pK_2^s	10.0	9.3	8.8
pH_{zpc}	8.4	8.5	8.5

Table IV. Physical and Chemical Properties of γ-Al_2O_3.

Ref [a]	size (nm)	SA (m^2/g) Method	EC (mmol/g) Method	SD (#/nm^2) Method	pH_{iep} pH_{zpc} Method	Surf Chem Model	pK_1 pK_2	C (F/m^2)
1	20 TEM	100 ± 15 BET			9.0 (?)			
2				12.5 crys calc				
3				14.8 crys calc				
4				13 crys calc				
5		100 BET (?)	1.4 tritium	8.5 EC ÷ SA				
6	20	100 BET	0.21 saturation	1.3 EC ÷ SA	8.7 titration	const capac	7.4 10.0	1.3(+) 13(-)
7	30	100 various	0.25 saturation	1.6 EC ÷ SA	8.3 titration	const capac	7.2 9.5	
8	30	100 various	0.1 saturation	0.6 EC ÷ SA	8.5 titr/EM	const capac	7.9 9.1	
9		82 BET			9.4 EM			
10		83.1 EGME	0.28 saturation	2.0 EC ÷ SA	7.5 titr 9.5 EM			
11		82 BET	0.728 F^- ads	5.3 EC ÷ SA	8.6 titr	const capac	7.64 9.7	2.0(+) 13(-)
this work	26 TEM	80 EGME	2.24 F^- ads/des	16.9 EC ÷ SA	8.4 titr 8.5 titr 8.5 titr	diffuse stern stern	6.8 10.0 7.7 9.3 8.2 8.8	6.0 5.4

[a] [1]Degussa, 1984. [2]Peri, 1965. [3]DeBoer et al., 1963. [4]Kipling and Peakall, 1957. [5]Kummert, 1979. [6]Kummert and Stumm, 1980. [7]Hohl and Stumm, 1976. [8]Huang and Stumm, 1973. [9]Bales, 1984. [10]Schultess and Sparks, 1987. [11]Davies, 1985.

were inputted into SURFEQL to determine the surface speciation at various pH values. SURFEQL is a computer code adapted from MINEQL (Westall et al., 1976) to solve equilibrium surface speciation calculations (Faughnan, 1981). Figure 1 shows the distribution of protonated, neutral and deprotonated surface sites for three different salt concentrations over the pH range 2-11 using a diffuse layer model. The Stern layer surface complexation models gave qualitatively similar results for the constants listed in Table III. The diffuse layer model presents a simple physical representation of the solid-liquid interface and has the least number of fitting parameters of the various electric double layer models. Also, because the diffuse layer capacitance is fixed by Gouy-Chapman theory, surface speciation at different ionic strengths can be obtained very easily. As can be seen in Figure 1, the neutral sites dominate the distribution over the pH range of most natural waters.

Procedure. (A) General. Unless specified otherwise, all experiments were performed at room temperature (23° C) in an open system (i.e., aqueous solutions were equilibrated with the surrounding atmosphere). The open system is a model which approximates the carbonate system of natural waters by equilibrating water with the atmosphere containing $CO_{2\,(g)}$ at a constant partial pressure (Stumm and Morgan, 1981). For waters which are in equilibrium with the atmosphere, the huge reservoir of $CO_{2\,(g)}$ imparts a significant buffering action above pH 7.

Aqueous solutions were prepared with distilled, deionized water (D_2H_2O) (Corning Mega-Pure™ System). Polycarbonate filters (Nuclepore, Pleasanton, CA) with pore sizes of 15 or 50 nm were used for all aluminum oxide particle separations.

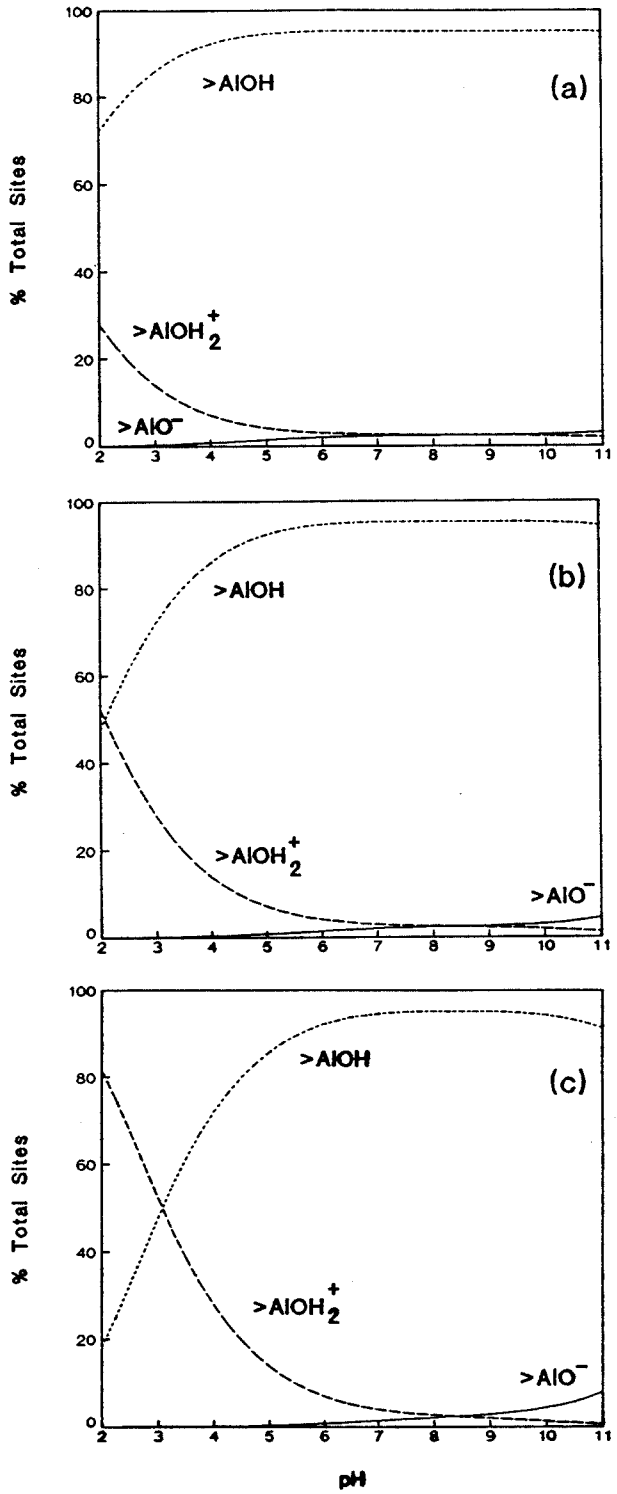


Figure 1. Surface speciation of Aluminum Oxide C from pH 2-11 using a diffuse layer model and the surface acidity constants from Table III. a) 0.001 M NaCl. b) 0.01 M NaCl. c) 0.1 M NaCl.

All glassware was cleaned by soaking in either 4 M HNO_3 or 4 M HCl, rinsing repeatedly with D_2H_2O, and drying in an oven at 110° C.

(B) Adsorption of Humic Substances. (1) pH Adsorption Envelope. The adsorption of humic and fulvic acid onto alumina was examined over a pH range of 4-11. Aliquots of concentrated alumina stock were diluted approximately 50-fold with D_2H_2O to give solid concentrations of ~400 mg/L. The diluted suspensions were sonicated for 2 hours to break up aggregates and were then purged with $N_{2\,(g)}$ while stirring for 6 hours until the pH stabilized. Aliquots of a 1 M NaCl stock and the respective DOM stocks were then added to obtain concentrations of 0.01 M NaCl and 4 mg/L DOM, and the suspensions were stirred for a few minutes. 30-mL aliquots were sequentially withdrawn from the suspensions, placed into 60-mL Boston round narrow mouth high density polyethylene bottles (VWR), and immediately spiked with varying amounts of either 0.1 N HCl or 0.1 N NaOH to adjust the pH. The bottles had been previously washed with 2 N HNO_3, rinsed 3 times with D_2H_2O and allowed to air dry before use.

The samples were mixed at 25°C and 200 rpm in a gyrotory water bath shaker (Model G76D, New Brunswick Scientific Co., Inc.) for 24 hours. The pH of each sample was measured and the particles were filtered using 50-nm pore filters which had been prewashed with 5 mL dilute (pH ~ 4) HCl. Because the initial concentration of DOM was relatively low, sampling the supernatant for residual DOM would not have given accurate measurements of adsorption (Davis, 1982). The filtrate, therefore, was discarded and the particles collected on the filters were rinsed

with 5 mL dilute HCl and resuspended in 10 mL of 0.01 M HCl. These samples were sonicated and mixed to yield uniform suspensions which were then injected directly into the TOC analyzer.

Aluminum oxide blanks (i.e., no humic material present) were prepared similarly in order to determine the solids concentration present in the adsorption experiment; the concentrations were determined gravimetrically as before. The blanks were also filtered and resuspended similarly to the samples in order to measure background TOC levels.

(2) Adsorption Isotherms. Adsorption isotherms of humic and fulvic acid on alumina were obtained at constant pH and ionic strength values. Very low solids concentrations (~20 mg/L) were used in order to maximize the adsorption density (i.e., obtain high surface coverages) and minimize the effects of particle coagulation in the adsorption experiments and, particularly, in the subsequent partitioning experiments (Chapter 4).

Dilute aluminum oxide suspensions (~200 mg/L) were prepared for use as working stocks in order to obtain consistent solids concentrations in the experiments. A working suspension was made by diluting 20 mL of concentrated alumina stock with D_2H_2O to a total volume of 1 L. The dilute suspension was sonicated briefly and allowed to stand overnight to equilibrate. After sonicating the suspension again for 30 minutes, the solids concentration was determined gravimetrically (3 replicates) by filtering 1 mL of suspension through preweighed 15-nm pore filters, drying the filters for 24 hours at 110°C, cooling in a desiccator, and weighing the filters again; the mass

of particles collected was determined by difference. Before use in adsorption experiments, a working suspension was sonicated for 30 minutes to resuspend the particles and break up aggregates.

Sample solutions were prepared by adding appropriate amounts of concentrated salt solution(s) and varying amounts of humic material stock solutions to D_2H_2O in Erlenmeyer flasks and adjusting the pH with 0.1 M HCl and/or 0.1 M NaOH. The samples were stirred until no further pH change was observed, indicating that they had reached equilibrium with the atmosphere. Aliquots of the working alumina suspension were then added to obtain the proper (calculated) solids concentration, and the pH was adjusted if necessary. The samples were then removed from the stirrer and the flasks were covered with parafilm and stored in the dark. The samples were not mixed during the adsorption period in order to avoid coagulation of the particles.

After the 24-hour adsorption period, the pH of each sample was checked and a 3-mL aliquot was removed for a subsequent partitioning experiment (Chapter 4). The remaining portion of each sample was filtered through a prewashed 50-nm pore filter, and the solids were rinsed on the filter with dilute HCl. Because the solid concentration was low in each sample, the extent of adsorption of humic substances was low, particularly at high DOM concentrations. The difference between the initial DOM concentration and that of DOM in the filtrate is not an accurate measure of the amount of humic material adsorbed by particles. The amount adsorbed, therefore, was determined directly. The filters were placed into 10 x 75 mm

Kimax® 51 borosilicate disposable culture tubes (VWR) containing 3 mL of 0.01 M HCl. The culture tubes were covered with parafilm and sonicated for a short time to resuspend the particles, and then were stored in the dark. After a few days, the particles had coagulated and settled from solution. The filters were then removed from the culture tubes and the samples were either analyzed for TOC or stored in the dark at 4°C for later analysis.

Before analyzing the samples for TOC, the culture tubes were sonicated for 10 minutes to resuspend the particles and make a uniform suspension. The suspensions were then injected directly into the TOC analyzer. Aluminum oxide blanks were prepared and treated similarly to the adsorption samples and were used to determine background TOC levels.

Data Treatment. The adsorption isotherms of humic substances on alumina at constant pH and ionic strength were modeled with a Langmuir isotherm equation:

$$\Gamma = \Gamma_m \frac{K_{ads} C}{1 + K_{ads} C} \tag{3.2}$$

where Γ is the adsorption density (mg humic material adsorbed/g Al_2O_3), Γ_m is the maximum adsorption density, C is the concentration of free humic material remaining in solution (mg humic material/L), and K_{ads} is an adsorption constant with units of inverse concentration. Langmuir-type isotherms have been used previously to describe the adsorption of humic substances on mineral surfaces (Tipping, 1981; Bales and Morgan, 1985). The Langmuir model was developed to describe systems

in which sorption leads to the deposition of a single layer of solute molecules on the surface of a sorbent (Weber et al., 1991). The model assumes that the energy of adsorption for each molecule is the same and is independent of surface coverage. It also assumes that adsorption occurs at specific sites on the sorbent and that the adsorbed solutes do not interact; thus, it is a site-specific model.

Many experimental adsorption isotherms are satisfactorily described by the Langmuir equation. However, a satisfactory fit of experimental data to the equation does not necessarily imply that the conditions forming the basis of the theoretical Langmuir model are fulfilled (Stumm and Morgan, 1981). For example, for the adsorption of humic substances on minerals, Γ_m is assumed to represent monolayer coverage of the solid by the humic material. In this case, monolayer coverage does not necessarily represent saturation of specific surface sites (surface hydroxyl groups) by direct coordination with humic carboxyl groups; instead, it is generally considered to represent total coverage of the surface area of the solid whereby each "humic molecule" physically occupies space on the surface.

The adsorption constant, K_{ads}, of the Langmuir model is related to the standard free energy of adsorption by the equation (Morel, 1983):

$$K_{ads} = \exp\left(\frac{-\Delta G^{o}_{ads}}{RT}\right) \tag{3.3}$$

Because the mechanism of adsorption for humic substances on mineral surfaces is most likely a combination of chemical (e.g., ligand exchange) and physical

(e.g., hydrophobic and/or electrostatic) bonding, the free energy of adsorption may be considered to consist of three parts:

$$\Delta G^{o}_{ads} = \Delta G^{o}_{chem} + \Delta G^{o}_{elec} + \Delta G^{o}_{hyd} \qquad (3.4)$$

where the components represent the intrinsic chemical, electrostatic and hydrophobic bonding energies, respectively. Experimentally, it is difficult or impossible to separate the energy of adsorption into its individual components (Stumm and Morgan, 1981). The problem becomes even less tractable for a complex, heterogeneous mixture of adsorbates such as humic substances. Because of the molecular heterogeneity of humic material, adsorption mechanisms and the corresponding adsorption energies (and individual component contributions) for humic molecules are not uniform. In this study, therefore, K_{ads} is considered to be only a measure of the affinity between the aluminum oxide surface and humic substances (Tipping, 1981).

The adsorption data was fit directly with equation (3.2) using a nonlinear least-squares curve-fitting program. The linearized form of the Langmuir model, obtained from the inversion of equation (3.2), was not used to fit the data because of the unwarranted emphasis it places on the data points at low solute concentration and low adsorption density. Because of experimental errors, the data in this region is generally less reliable than at higher solute concentrations.

RESULTS AND DISCUSSION

The adsorption of humic substances on alumina was investigated both as a function of pH for fixed NOM concentrations (adsorption envelopes) and as a function of NOM concentration at fixed pH values (adsorption isotherms).

The amount of humic and fulvic acid adsorbed decreased with increasing pH (Figure 2). At relatively high solid concentrations (400 mg/L), the adsorption density for humic acid ranged from 10 mg-HA/g-alumina (~100% adsorbed) at pH 4 to approximately half that value at pH 11. Fulvic acid showed a similar trend with an adsorption density of 8 mg/g (80% adsorbed) at pH 4.6 and less than 2 mg/g (~19% adsorbed) at pH 11. Decreases in adsorption density with increasing pH have been reported for other natural organic material, as well as for simple organic acids (Kummert and Stumm, 1980; Davis, 1980, 1982; Davis and Gloor, 1981; Tipping, 1981; Jardine et al., 1989; Murphy et al., 1990).

The adsorption of fulvic acid was observed always to be less than that for humic acid at all pH values (Figure 2), and appeared to show more dependence on pH than did the humic acid adsorption. The calculated surface coverage of the alumina particles was extremely low (< 10%) because the high solid concentrations in the samples either depleted the NOM or promoted coagulation of the particles, thereby decreasing the actual surface area available for adsorption.

Figures 3 and 4 show the adsorption isotherms of humic and fulvic acid, respectively, for varying aqueous chemistry conditions. At each combination of fixed pH and ionic strength, the adsorption density increased with increasing total NOM

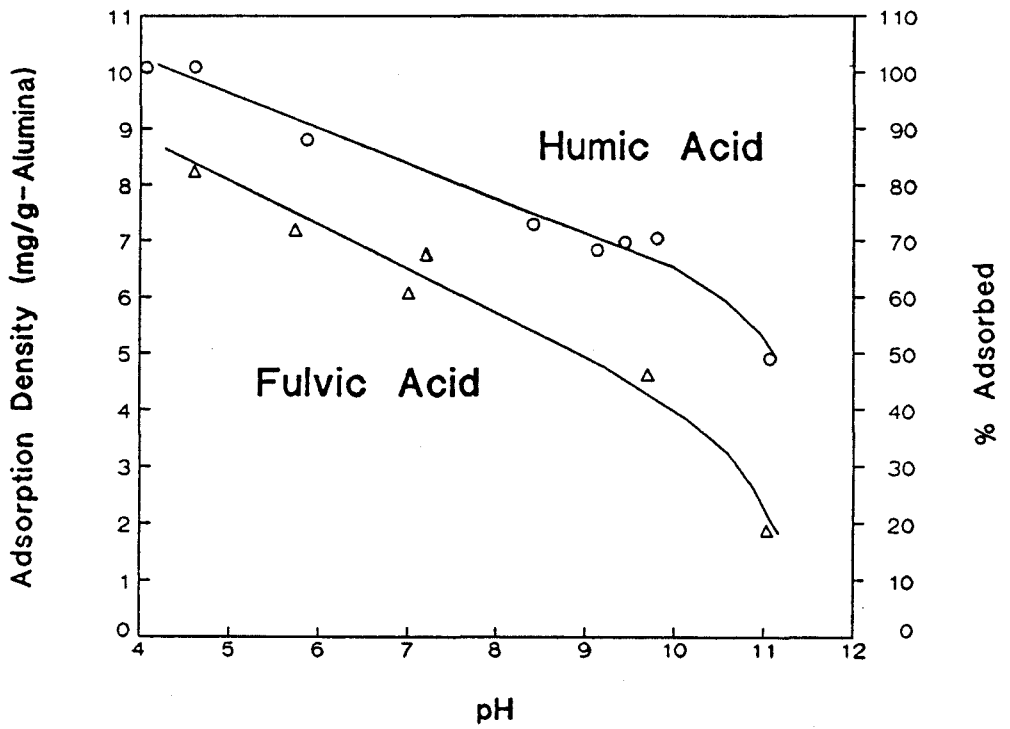


Figure 2. Adsorption envelopes on alumina for Suwannee River humic substances in 0.01 M NaCl at 25°C. Solid concentrations were 400 mg/L and initial humic and fulvic acid concentrations were 4 mg/L.

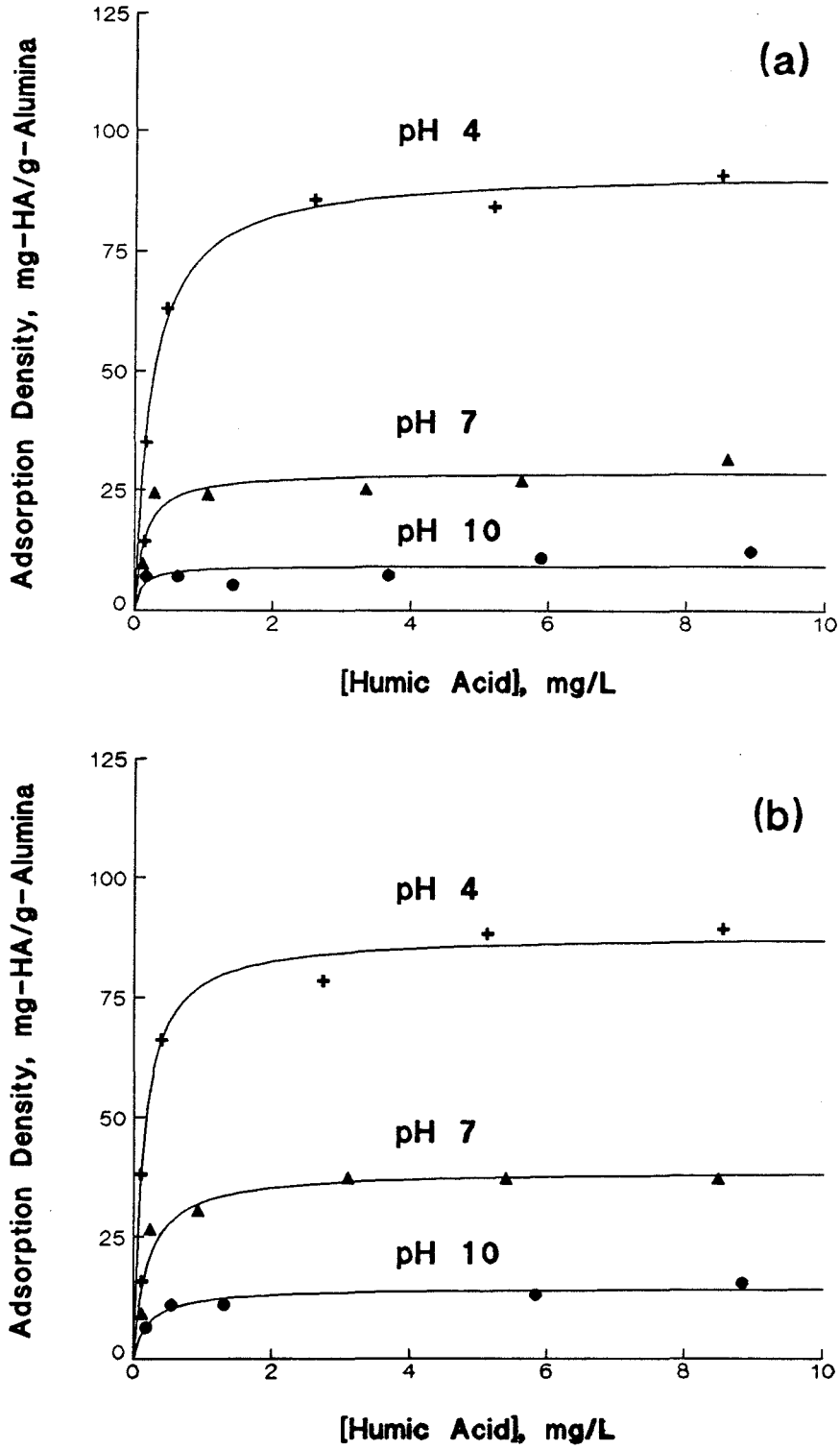


Figure 3. Adsorption isotherms of humic acid on alumina. Solid concentrations were 20 mg/L. a) 0.001 M NaCl. b) 0.01 M NaCl.

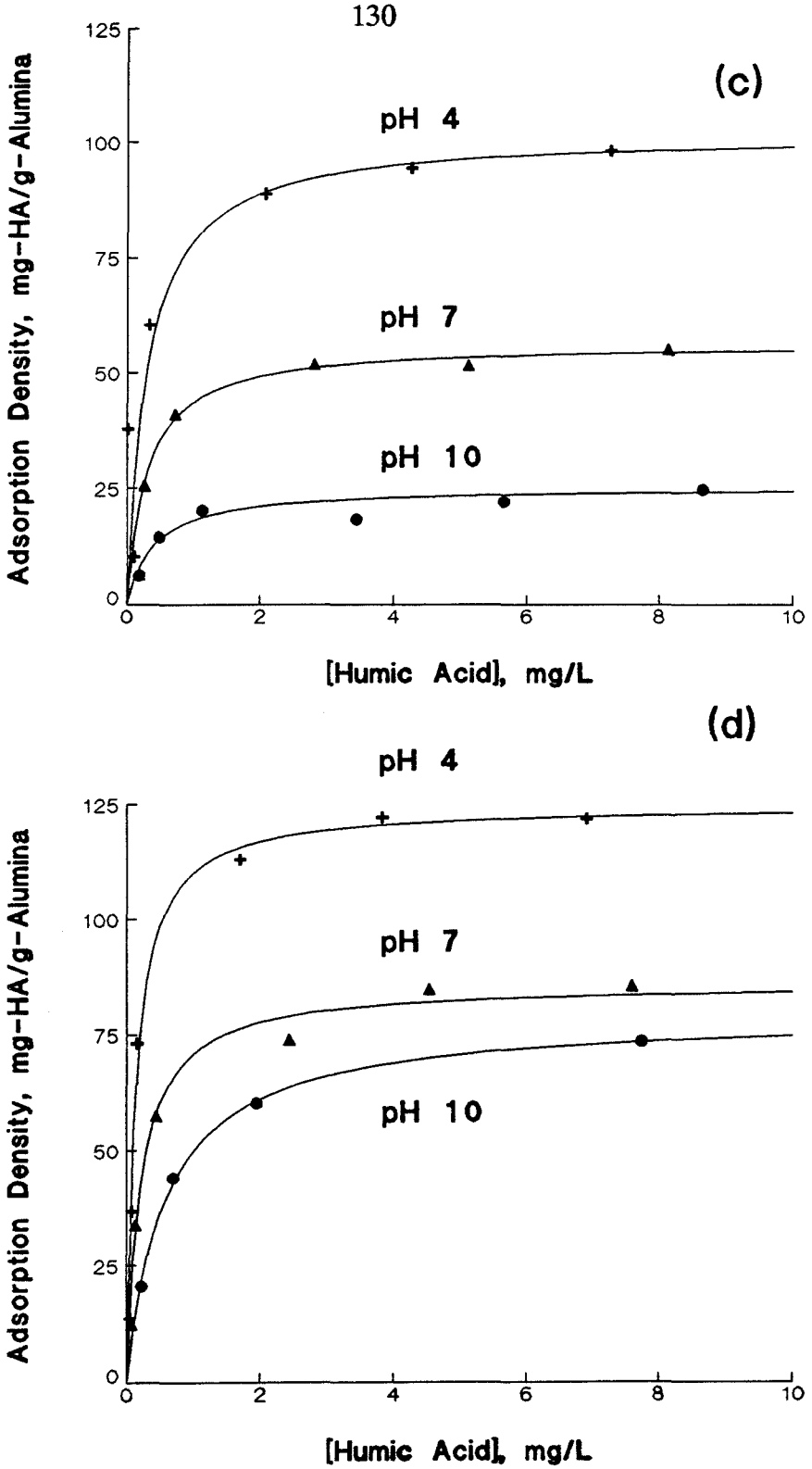


Figure 3. Adsorption isotherms of humic acid on alumina. Solid concentrations were 20 mg/L. c) 0.1 M NaCl. d) 1 mM Ca^{2+} and 0.1 M total ionic strength.

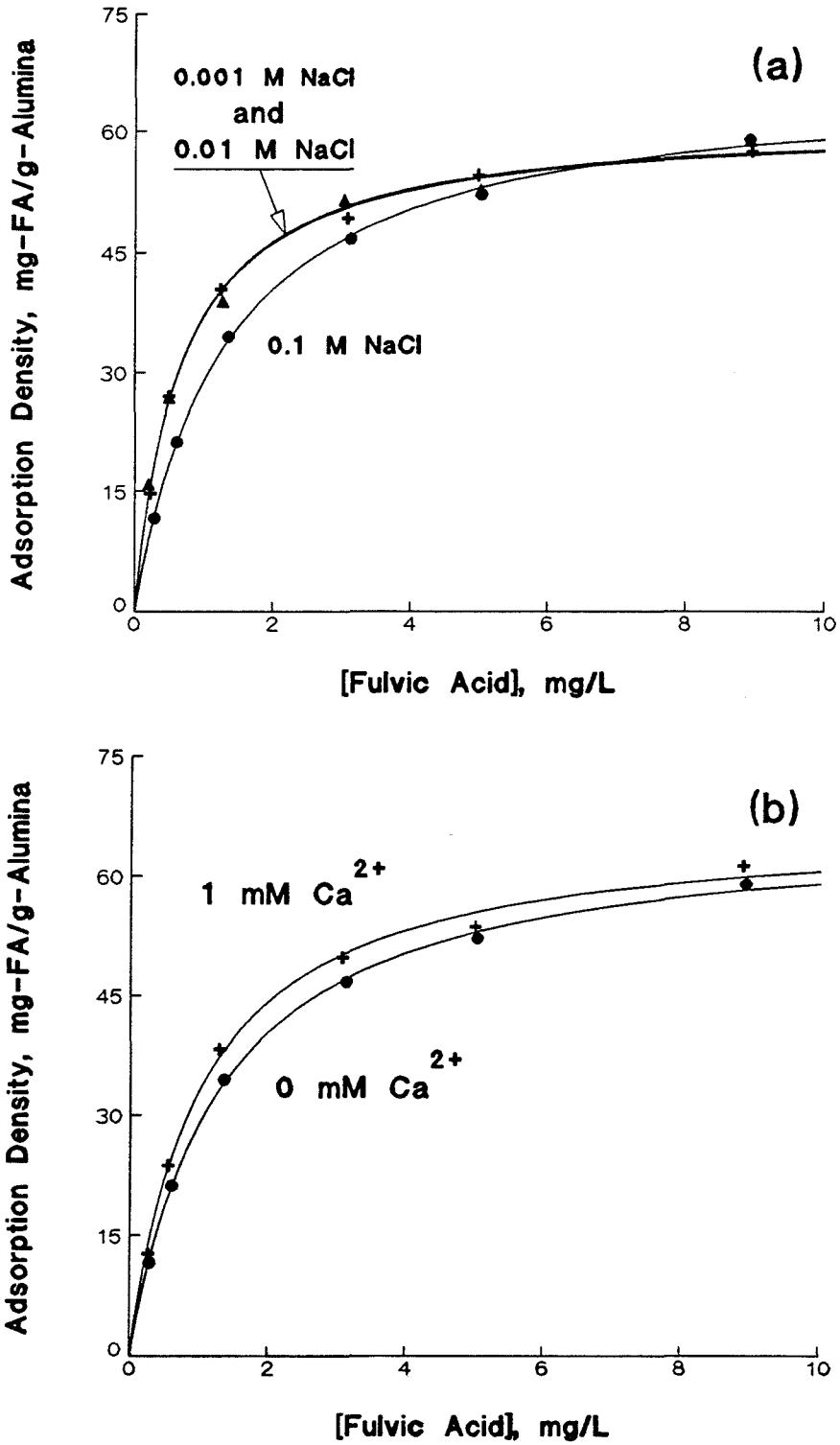


Figure 4. Adsorption isotherms of fulvic acid on alumina. Solid concentrations were 20 mg/L. a) pH 4. b) pH 4 and 0.1 M total ionic strength.

in the system until a plateau was reached at maximum adsorption. Because the alumina concentrations were low in the isotherm experiments, the adsorption densities observed were significantly higher than those obtained in the adsorption envelope studies. At pH 4, the surface coverage of the alumina particles approached 100% with humic acid, while the maximum surface coverage using fulvic acid was calculated to be less than 40%.

The adsorption isotherms in Figures 3 and 4 were fit with equation (3.2). Values for the Langmuir parameters K_{ads} and Γ_m are listed in Table V for the various systems. In all cases, the observed isotherms showed a reasonably good fit to the Langmuir equation. Langmuir-type isotherms have been observed previously for humic material adsorption on mineral surfaces and soils (Tipping, 1981; Bales and Morgan, 1985; Murphy et al., 1990; Jardine et al., 1989).

Complexes formed between mineral surfaces and NOM are not completely understood because of the heterogeneity and complexity of organic matter. For mineral surface reactions, the most accessible characteristic of humic material is its functional group behavior; stereochemistry is also of great importance, but this characteristic is relatively poorly defined in the absence of complete structural information (Sposito, 1984, 1989).

The mechanisms by which humic substances are thought to adsorb to mineral surfaces and soils have been deduced from studies in which model organic compounds of known molecular structure and possessing functional groups

Table V. Langmuir Isotherm Parameters.[a]

	Humic Acid		Fulvic Acid	
	K_{ads}	Γ_m	K_{ads}	Γ_m
0.001M NaCl				
pH 4	4.25	91.81	1.51	61.42
pH 7	7.34	28.81	ND [b]	ND
pH 10	9.78	9.16	ND	ND
0.01M NaCl				
pH 4	7.47	88.03	1.52	61.59
pH 7	4.91	38.77	ND	ND
pH 10	4.53	14.36	ND	ND
0.1M NaCl				
pH 4	4.56	99.74	0.76	66.89
pH 7	3.42	56.38	ND	ND
pH 10	2.57	21.56	ND	ND
1mM Ca^{2+} [c]				
pH 4	7.58	124.51	0.98	66.87
pH 7	4.72	85.84	ND	ND
pH 10	1.70	79.13	ND	ND

[a] From equation (3.2). Units are K_{ads} (L/mg), Γ_m (mg/g).
[b] ND, not determined. [c] 0.1 M total ionic strength.

characteristic of NOM were reacted with hydrous oxide surfaces (e.g., Kummert and Stumm, 1980). Descriptions of these mechanisms and their applicability to NOM adsorption have been discussed by Sposito (1984, 1989). The principal mechanisms thought to be operative in the adsorption of humic material on mineral surfaces include anion exchange, bridging (water or cation), hydrophobic bonding (i.e., repulsion of hydrophobic moieties from water and/or van der Waals forces), and ligand exchange.

Of the principal adsorption mechanisms, the most important is considered to be ligand exchange. Ligand exchange refers specifically to direct bond formation between a carboxylate group and either Al(III) or Fe(III) in minerals possessing inorganic hydroxyl groups (Sposito, 1984, 1989). The chemical bonds formed in the inner-sphere complexes are stronger than the electrostatic bonds involved in anion exchange or in the two bridging mechanisms. Evidence for ligand exchange in carboxylate adsorption reactions of humic substances with mineral surfaces is abundant though indirect (e.g., Tipping, 1981; Davis, 1982); adsorption is thought to be analogous to inorganic oxyanion ligand-exchange reactions.

Ligand-exchange complexation reactions have been observed in adsorption studies of organic acids on hydrous oxide surfaces. The most convincing arguments for inner-sphere complex formation are those from spectroscopic studies. Stumm and coworkers (Furrer and Stumm, 1986; Hering and Stumm, 1991) have examined the ligand-enhanced dissolution of alumina and have used these studies and fluorescence spectroscopic information to deduce that adsorbed organic acids form inner-sphere

complexes with Al(III). Yost et al. (1990) studied the adsorption of salicylate on goethite using an in situ cylindrical internal reflection (CIR) FTIR spectroscopic method. At low surface coverages the salicylate formed a chelate structure in which one carboxylic oxygen and the ortho phenolic oxygen bound one Fe(III) atom of the goethite surface (inner-sphere complex). At higher surface coverages the chelate complex coexisted with interfacially-bound salicylate ions which were presumably held via an electrostatic outer-sphere complex or a weak bridging bidentate complex.

Adsorption of humic substances by a ligand-exchange mechanism is thought to proceed by the following sequence (Sposito, 1984, 1989; Murphy et al., 1990):

$$>SOH + H^+ \rightleftharpoons >SOH_2^+ \tag{3.5}$$

$$>SOH_2^+ + Hu\text{-}C(O)O^- \rightleftharpoons >SOH_2^+O^-C(O)\text{-}Hu \tag{3.6}$$

$$>SOH_2^+O^-C(O)\text{-}Hu \rightleftharpoons >SOC(O)\text{-}Hu + H_2O \tag{3.7}$$

where >SOH represents a surface hydroxyl group on the mineral (S is the metal cation Al(III) or Fe(III)) and Hu-COO$^-$ represents the humic carboxyl group. The protonation step in equation (3.5) is thought to make the surface hydroxyl group more exchangeable, but may not be necessary if the concentration of humic carboxyl groups is sufficiently high (Sposito, 1984). Humic carboxyl groups may then form outer-sphere complexes with the protonated surface hydroxyl groups (equation (3.6)), and ligand exchange occurs in equation (3.7) in which Hu-COO$^-$ replaces OH_2 and forms an inner-sphere complex with the metal cation.

The pH dependence observed in Figure 2 has been attributed previously to a ligand-exchange mechanism (Tipping, 1981; Davis, 1982; Murphy et al., 1990). In general, the amount of NOM adsorbed on mineral surfaces and soils tends to decrease as the pH increases above ~4. The protonation step (equation (3.5)) is partly responsible for this observation; as the pH increases, the concentration of protonated surface hydroxyls decreases. Another factor in the effect of pH on the adsorption of oxyanions is the pK_a of the conjugate Brønsted acid. The concentration of oxyanions increases with increasing pH, thus favoring more adsorption at pH values above the pK_a. The adsorption envelope, therefore, is the resultant of a competition for H^+ by the anion and the mineral surface and may be characterized by the mineral pH_{zpc} and the pK_a of the sorbate (Sposito, 1989). If several protonated species of an oxyanion exist, such as for humic substances, the adsorption envelope shows a monotonic decline with increasing pH value. The ligand-exchange mechanism (equations (3.5)-(3.7)) is consistent with these observations in that it predicts decreasing adsorption as the protonation of the surface decreases but increasing adsorption as the protonation of the oxyanion decreases (Sposito, 1989).

The effect of pH on the extent of adsorption may also result from mechanisms other than ligand exchange. Similar adsorption envelopes and pH dependence should be exhibited by an anion-exchange mechanism. Anion exchange can be represented by the following reaction:

$$>SOH_2^+Cl^- + Hu\text{-}C(O)O^- \rightleftharpoons >SOH_2^+O^-C(O)\text{-}Hu + Cl^- \qquad (3.8)$$

in which a humic carboxyl group replaces an anion (chloride in this example) previously bound in an outer-sphere complex. This mechanism is not observed often because of the weakness of the electrostatic bonds involved, but may be prominent in acidic systems with metal oxides as sorbents (Sposito, 1984, 1989). For example, Jardine et al. (1989) observed that ~25% of the total DOC adsorbed on a soil sample could be attributed to an anion-exchange mechanism.

From the data in Figures 2 through 4, it is not possible to validate or refute the presence of an anion-exchange mechanism at low pH values ($pH < pH_{zpc}$). In a NaCl medium, it may be argued that increases in the Cl^- concentration should decrease the adsorption of humic substances for an anion-exchange mechanism in accordance with equation (3.8). From the data in Table V (Γ_m versus [NaCl]), therefore, fulvic acid would not appear to adsorb by anion exchange. Humic acid does show an initial decrease in Γ_m when the NaCl concentration is increased from 1 to 10 m$\underline{M}$, but then Γ_m increases for 0.1 $\underline{M}$ NaCl. Thus the presence or absence of anion exchange for humic acid can not be determined from these data.

The above analysis is questionable, however, in determining the presence of an anion-exchange mechanism for humic substances. Increases in electrolyte concentrations can also affect adsorption through electrostatic interactions, such as decreasing the repulsion between uncomplexed carboxyl groups of adsorbed humic material. Decreases in adsorption with increasing electrolyte may be attributed to mechanisms other than anion exchange. For example, Stone (1989) studied the hydrolysis of the anionic carboxylic acid ester monophenyl terephtalate (MPT^-) in the

presence of alumina and concluded that the adsorption of MPT^- on alumina could be fully accounted for using an inner-sphere surface complex formation model. The decrease in MPT^- adsorption with increasing Cl^- concentration was attributed to the loss of protonated hydroxyl sites because of outer-sphere complex formation with Cl^-.

At high pH values, an anion-exchange mechanism cannot account for the observed adsorption of humic substances on alumina (Figures 2-4). The significant amount of adsorption at pH values > pH_{zpc} implies that other mechanisms of adsorption are operative in the system. The most plausible mechanisms for NaCl electrolyte solutions are ligand exchange and hydrophobic bonding. Of these two, ligand exchange is considered to be more important for the reasons discussed above. However, there may be situations in which hydrophobic bonding is significant.

Jardine et al. (1989), for example, examined the adsorption of DOC on a soil sample at two different temperatures and observed that the adsorption was relatively insensitive to temperature. The reaction was slightly endothermic (4 to 8 kJ/mol), as evidenced by higher amounts of adsorption at the higher temperature. Because ligand-exchange reactions generally are highly exothermic (necessary to offset the decrease in solute entropy upon adsorption), they concluded that ligand exchange was not a plausible mechanism. The absence of an increase in pH accompanying adsorption further supported their contention that ligand exchange was insignificant [equation (3.5)]. Instead, Jardine et al. (1989) suggested the DOC adsorption mechanism was physical adsorption driven by favorable entropy changes (i.e., hydrophobic bonding). They strengthened this argument by examining the

adsorption of fractionated DOC solutions. Of the total DOC adsorbed by the soils, over 80% was hydrophobic organic solutes.

Hydrophobic bonding has been discussed in some detail in Chapter 2 and has been thoroughly reviewed elsewhere (Tanford, 1980; Israelachvili, 1985; Voice and Weber, 1983). Van der Waals dispersion interactions may be as important to NOM-mineral associations as they are to organic compound-NOM reactions (Sposito, 1989). The van der Waals bonding forces between polymeric humic material and atoms in a mineral surface can be quite strong and relatively long-range (i.e., greater than atomic distances). The effects of van der Waals interactions are especially apparent when ionization of acidic functional groups on large organic molecules is suppressed, as for solutions of high ionic strength or when the pH value is such as to make the net charge on the molecules vanish (Sposito, 1984).

Hydrophobic bonding similar to that observed by Jardine et al. (1989) may partly explain the fractionation and preferential adsorption of NOM that has been observed in previous studies. Davis and Gloor (1981) found that adsorption of NOM by alumina increased with the molecular weight of the organic material. Murphy et al. (1990) found that the amount of humic substances adsorbed on a specific mineral substrate was positively correlated to the aromaticity and molecular weight and negatively correlated to the O/C ratio (i.e., polarity) of the organic material. Humic acids were found to be more strongly adsorbed than fulvic acids, in agreement with the observed correlations. The combined results indicate, therefore, that the more hydrophobic NOM (humic acid) adsorbed preferentially relative to

more hydrophilic NOM (fulvic acid).

Comparable results were observed in this study, which utilized humic materials similar to some examined by Murphy et al. (1990). The adsorption density for humic acid was always higher than that for fulvic acid at the same pH and ionic strength (Figures 2-4, Table V). In Tables I and II, it is observed that humic acid is larger (1100 versus 800 daltons), more aromatic (f_a of 0.42 versus 0.28) and less polar (O/C of 0.54 versus 0.57) than fulvic acid.

Murphy et al. (1990) concluded that humic substances with higher molecular weight are more strongly adsorbed because their carboxyl group content is greater on a molar basis. However, at least for Suwannee River humic and fulvic acid, this conclusion is not valid because the carboxyl content of the two humic substances is similar (~5 COO^- groups per molecule). Likewise, the use of a ligand-exchange mechanism by Murphy et al. (1990) to describe all the observed humic material adsorption in their study is questionable, particularly for the peat humic acid/hematite system. The extent of adsorption for peat humic acid did not decrease with increasing pH, as would be predicted for a ligand-exchange mechanism. Instead, a hydrophobic-bonding mechanism appears to be operative, which accounts for at least a fraction of the adsorption.

From the discussion above, it becomes obvious that separating the energy of adsorption into its individual components [e.g., equation (3.4)] is very difficult because the mechanisms of adsorption for NOM on mineral surfaces are not well understood. In natural systems, it is plausible that no one adsorption mechanism

operates entirely in the absence of other mechanisms. One or more of the principal adsorption mechanisms and possibly others are expected to be operative when NOM reacts with mineral surfaces (Sposito, 1984). For instance, it is expected that protonation plays a role in adsorption in acidic media, as does negative adsorption when the net mineral surface charge is negative.

Although the adsorption mechanisms in this study are not clearly defined, a qualitative interpretation of the adsorption processes can be made utilizing the Langmuir isotherm parameters (Table V). Using this methodology, Tipping (1981) was able to elucidate the adsorption mechanism of an aquatic humic substance onto iron oxides.

The data for humic acid in Table V show that the decrease in the extent of adsorption with pH (Figure 2) is due mainly to a decrease in the number of available adsorption sites (i.e., Γ_m). As discussed earlier, this observation is consistent with both a ligand-exchange mechanism, as well as an anion-exchange mechanism, at lower pH values. At higher pH values the adsorption cannot be attributed to anion exchange. Therefore, the observed decrease with pH is due to ligand exchange. For NaCl concentrations of 10 mM and 0.1 M, the decrease in adsorption with pH is also caused by a decrease in the affinity between the humic acid and the alumina surface (i.e., K_{ads}). Tipping (1981) attributed this to increasing electrostatic repulsion between humic substances and the mineral due to a progressive increase in deprotonated surface hydroxyl groups ($>FeO^-$).

This argument, however, does not explain the results observed at 1 mM NaCl

concentrations. As the pH increases at this ionic strength, K_{ads} also increases. The only plausible explanation for this observation appears to be the presence of a cation-bridging adsorption mechanism. In this mechanism, Na^+ would be attracted to the surface as the pH increases because of the increase in $>AlO^-$ groups; the humic carboxyl groups would then attach directly to the bound Na^+. The formation of $>AlO^-Na^+$ becomes increasingly significant above pH 7 (Stone, 1989). However, the total number of adsorption sites would not increase significantly because of the relatively small fraction of $>AlO^-$ sites that are present even at pH 10 (Figure 1a).

Cation bridging cannot explain, however, the transition that occurs between 1 mM and 10 mM NaCl solutions. For example, the concentration of $>AlO^-Na^+$ groups increases with increasing NaCl concentrations (Stone, 1989); thus, cation bridging should be even more important at higher NaCl concentrations. The observed K_{ads} values, therefore, must result from the different adsorption mechanisms which are present and interact in complex fashions. The enhanced cation bridging expected at higher NaCl concentrations, for example, may be offset by the increased electrostatic repulsion between uncomplexed carboxylate groups in the adsorbed layer as the surface coverage increases. Also, it is uncertain how hydrophobic bonding may affect the affinity observed here.

For fixed pH values, changes in NaCl concentration also affect the adsorption of humic substances. Increases in the adsorption of humic acid with increasing NaCl concentration (Figure 3a,b,c; Table V) are attributed mostly to an increase in the number of available adsorption sites. At all pH values, Γ_m increases with an increase

from 1 mM to 0.1 M NaCl, while K_{ads} generally decreases. The increase in electrolyte at pH 4 and 7 increases the number of protonated surface hydroxyls (Figure 1a,b,c); ligand exchange is thus enhanced by additional adsorption sites. At pH 10, the increase in NaCl concentration enhances cation bridging and decreases the electrostatic repulsion between the alumina surface and humic material, as well as between unbound humic carboxyl groups. The adsorption of fulvic acid at pH 4 follows a similar trend with increasing NaCl concentration (Figure 4a, Table V).

In basic media (pH > 7), the presence of bivalent cations introduces another adsorption mechanism relative to electrolytes containing only monovalent cations. The additional mechanism now postulated to occur in basic media is water bridging, a process similar to the cation bridging mechanism discussed earlier. The major difference between the two is the presence or absence of water molecules solvating the exchangeable cation at the humic carboxyl adsorption site. Whether water bridging or cation bridging occurs during the adsorption of an anion by a surface bearing solvated exchangeable cations depends on the relative Lewis base character of the functional group and the relative Lewis acid character of the exchangeable cation (Sposito, 1984, 1989). For example, carboxylate groups on humic substances may adsorb on mineral surfaces through cation bridging in the presence of Na^+ and through water bridging when Ca^{2+} is present.

In addition to water bridging, bivalent cations most likely modify other adsorption mechanisms at all pH values. For example, Ca^{2+} alters electrostatic interactions relative to NaCl solutions and may also form soluble complexes with

natural organic ligands.

Tipping (1981) found that the adsorption of aquatic humic substances by goethite at fixed ionic strength approximately doubled in the presence of bivalent cations at a total concentration of 3.3×10^{-4} M (61.5 μM Mg^{2+}, 263 μM Ca^{2+}). The extent of adsorption still decreased with increasing pH, but the isotherm did not conform to the Langmuir equation because of the additional adsorption capacity. He proposed that adsorption of organic material was increased by the formation of complexes with the bivalent cations which then allowed more humic molecules to adsorb to the oxide surface. Since the effect was seen at pH 6, it is unlikely that water bridging was contributing extra adsorption sites. Also, it was postulated that the bivalent cations reduced the electrostatic repulsion between humic molecules at the goethite surface more effectively than did the monovalent cations and protons.

Davis (1982) studied the effect of varying Ca^{2+} concentrations at constant ionic strength (0.01 M) on DOC adsorption by alumina. Significant changes were observed under acidic and alkaline conditions at a Ca^{2+} concentration of 4×10^{-3} M relative to a NaCl solution. For pH $<$ 7, the amount of DOC adsorbed was less than that for the NaCl solution, while at pH values $>$ 7 the presence of Ca^{2+} enhanced adsorption. At lower Ca^{2+} concentrations, smaller, but similar effects were observed.

The effect of Ca^{2+} on the adsorption of humic and fulvic acid by alumina was investigated in this study. The presence of 1 mM Ca^{2+} (0.1 M total ionic strength) increased the adsorption of humic acid at all pH values relative to NaCl solutions, but had little effect on the adsorption of fulvic acid at pH 4 (Figures 3d and 4b,

Table V). Despite the increase in adsorption for humic acid, Langmuir-type isotherms were observed in the presence of Ca^{2+} for all of the studies, in contrast to the observations of Tipping (1981).

In the presence of Ca^{2+}, the enhanced adsorption observed for humic acid at pH 10 resulted mainly from an increase in adsorption sites (Table V) which were created through water bridging. At pH 4 and 7, however, the increased adsorption of humic acid most likely occurred because of a decrease in electrostatic repulsion between unbound humic carboxyl groups. Since the concentration of deprotonated surface hydroxyl groups is relatively low at these pH values, the binding of Ca^{2+} by surface adsorption sites at pH 7 and, particularly, at pH 4 is unlikely. This argument was verified by the experimental observation that Ca^{2+} was bound significantly to the bare aluminum oxide particle surfaces only at pH 10. The argument is also supported by the data in Table V; while the presence of Ca^{2+} increases Γ_m for humic acid at pH 4 and 7 approximately the same amount, the increase in Γ_m at pH 10 is significantly higher and approaches the value observed at pH 7.

The relative importance of different adsorption mechanisms changes with solution composition for a particular humic material, as has been discussed. The absence of enhanced adsorption of fulvic acid in the presence of Ca^{2+} at pH 4 indicates that different adsorption mechanisms are operative for humic and fulvic acid under similar solution conditions or, more accurately, that the mechanisms have different relative importance in humic versus fulvic adsorption. Other differences between humic and fulvic adsorption which have been previously discussed seem to

support this argument:

(1) The adsorption of fulvic acid appears to show more dependence on pH than does humic acid adsorption (Figure 2).

(2) Despite having similar functional groups and carboxyl contents, the affinity between humic acid and alumina is much larger than that between fulvic acid and alumina for the same pH and ionic strength (K_{ads} in Table V).

(3) The increased adsorption of humic acid relative to fulvic acid agrees with predictions from correlations based on aromaticity, molecular weight and polarity (i.e., parameters describing hydrophobicity).

It was instructive, therefore, to investigate more closely the differences between humic and fulvic acid adsorption on alumina. Although the adsorption of humic and fulvic acid both followed Langmuir-type isotherms, the data at lower concentrations tend to be minimized by plots such as Figures 3 and 4. By plotting measured adsorption densities against the values "predicted" from the Langmuir fit, linear graphs can be generated to observe how well the Langmuir equation fits each data point of the adsorption isotherm (Figure 5).

The slope of each line in Figure 5 is unity by definition. In Figure 5b, the Langmuir equation fits every data point extremely well for the fulvic acid adsorption data presented. All other fulvic acid adsorption isotherms had equally good fits to Langmuir isotherms. For humic acid (Figure 5a) the higher adsorption densities showed a similarly good fit to the Langmuir equation. However, the lowest measured adsorption density data point was lower than that predicted from the Langmuir

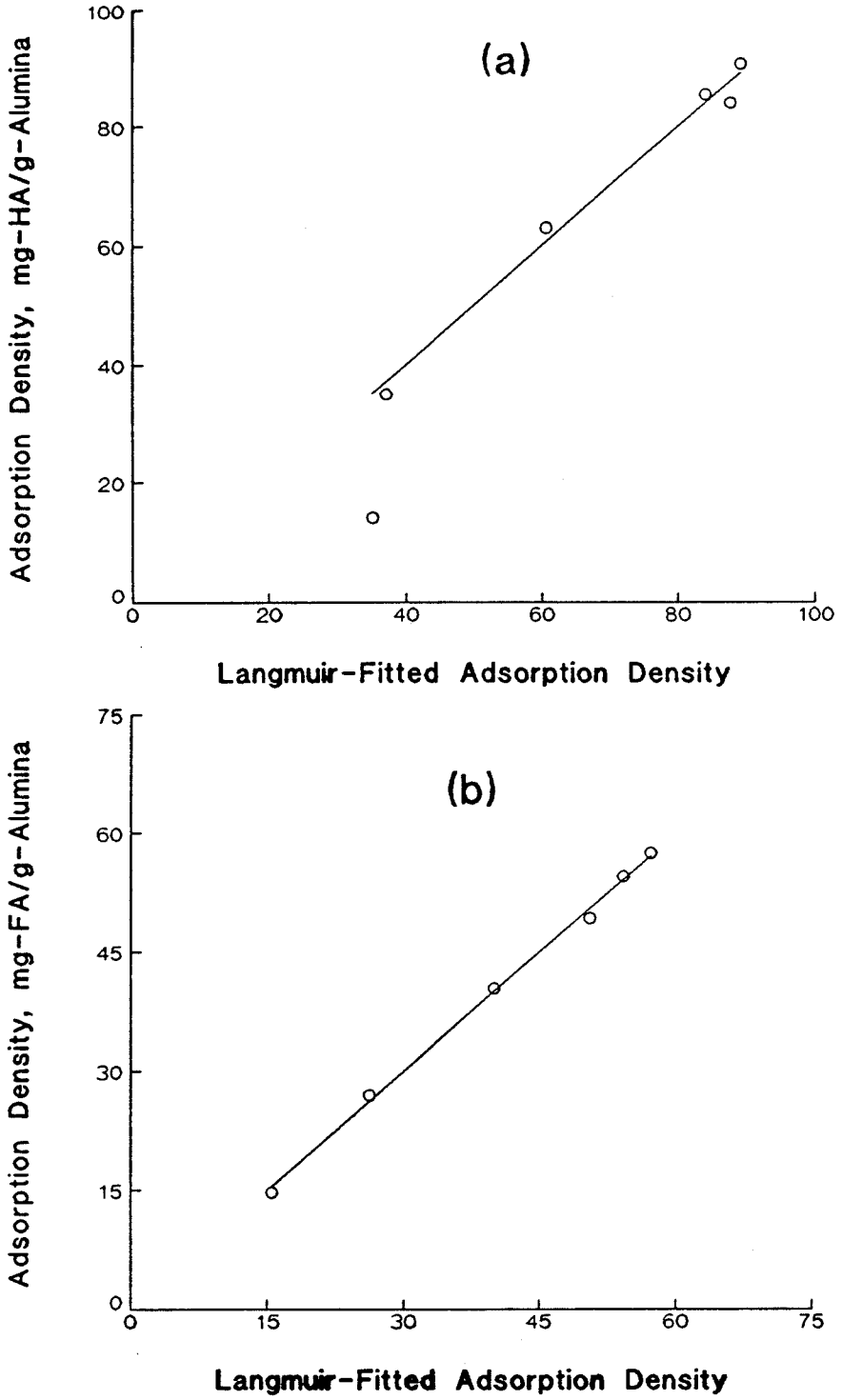


Figure 5. Humic material adsorption on alumina in 0.001 M NaCl at pH 4. Plots show measured adsorption densities versus adsorption densities calculated from the fitted Langmuir models. The slope of each line is unity (the values from the Langmuir model are plotted against themselves). a) Humic acid. b) Fulvic acid.

equation. Upon examining other adsorption data sets with this technique, it was observed that all humic acid isotherms at pH 4 and 7 consistently had similar deviations from the Langmuir equation for the lowest adsorption density data point. This deviation was observed for all NaCl concentrations, as well as in the presence and absence of Ca^{2+}. At pH 10, however, the figures looked like those for fulvic acid; the Langmuir equation fit each point equally well.

By presenting the isotherm data as the extent of adsorption versus initial NOM concentration, the same grouping of experiments as above is observed (Figures 6 and 7). In Figure 7, the extent of fulvic acid adsorption continually decreases as the initial fulvic acid concentration is increased. This is observed for all NaCl concentrations, as well as in the presence of Ca^{2+}. Similar decreases are observed for humic acid adsorption at pH 10 (Figure 6c,d). The plots are different, however, for humic acid at pH 4 and 7 (Figure 6a,b,d). The extent of adsorption in these studies increases initially before decreasing monotonically with increasing humic acid concentration.

The results observed for humic acid in Figure 6 appear to show that some type of cooperative adsorption occurs between humic acid molecules at low surface coverage at pH 4 and 7. A preliminary adsorption study at very low initial humic acid concentrations was re-evaluated to examine if cooperative adsorption could be observed at low surface coverages. The results of this experiment are shown in Figure 8. The classical "S-shaped" isotherm is indeed observed for humic acid at initial concentrations below 0.5 mg/L.

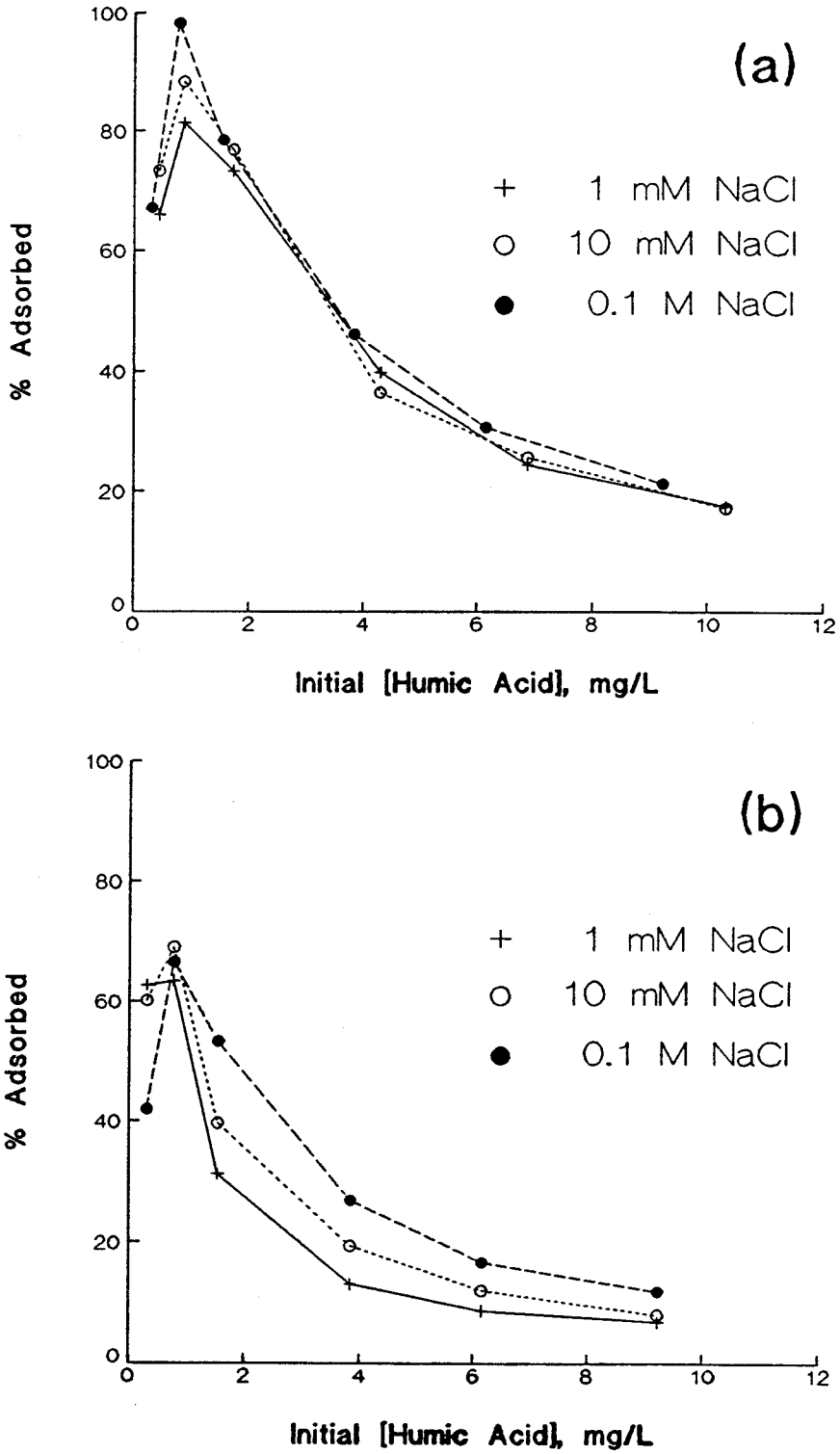
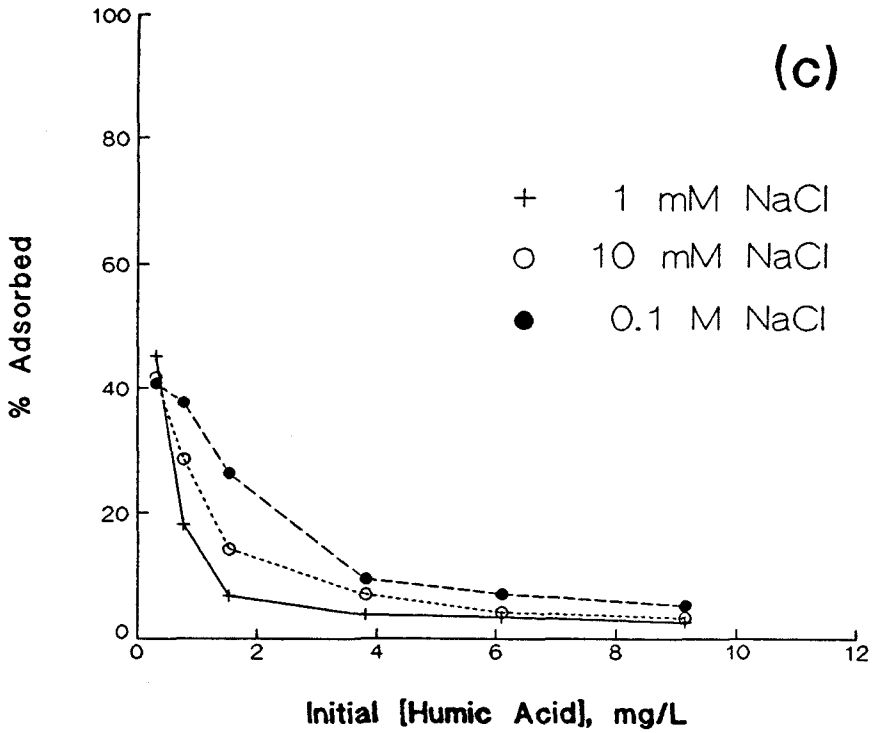


Figure 6. Fractional adsorption of humic acid on alumina versus initial humic acid concentration. Solid concentrations were 20 mg/L. a) pH 4. b) pH 7.



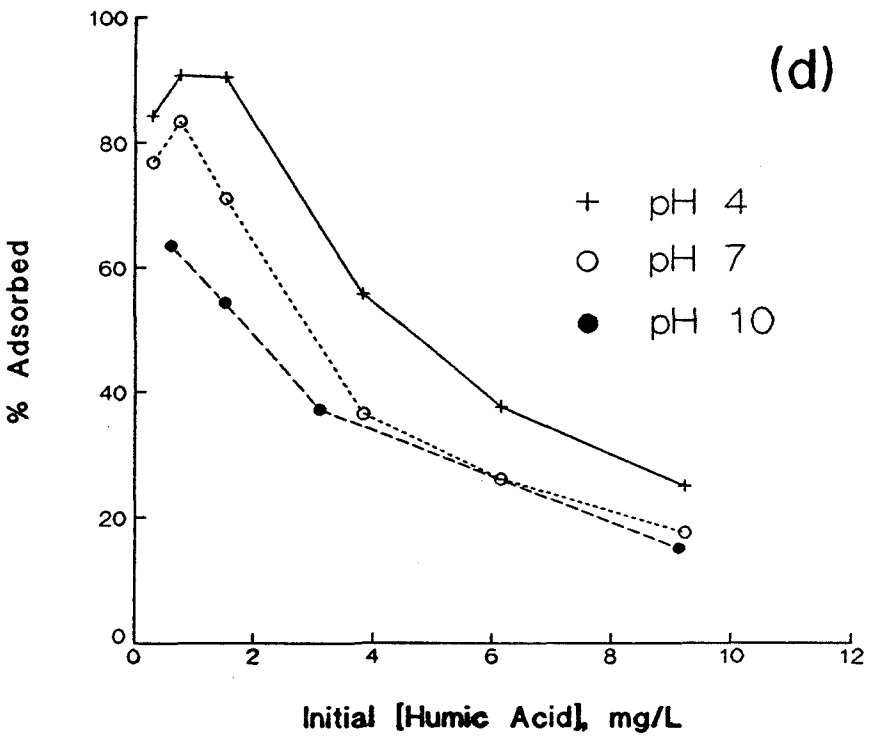


Figure 6. Fractional adsorption of humic acid on alumina versus initial humic acid concentration. Solid concentrations were 20 mg/L. c) pH 10. d) 1 mM Ca^{2+} and 0.1 M total ionic strength.

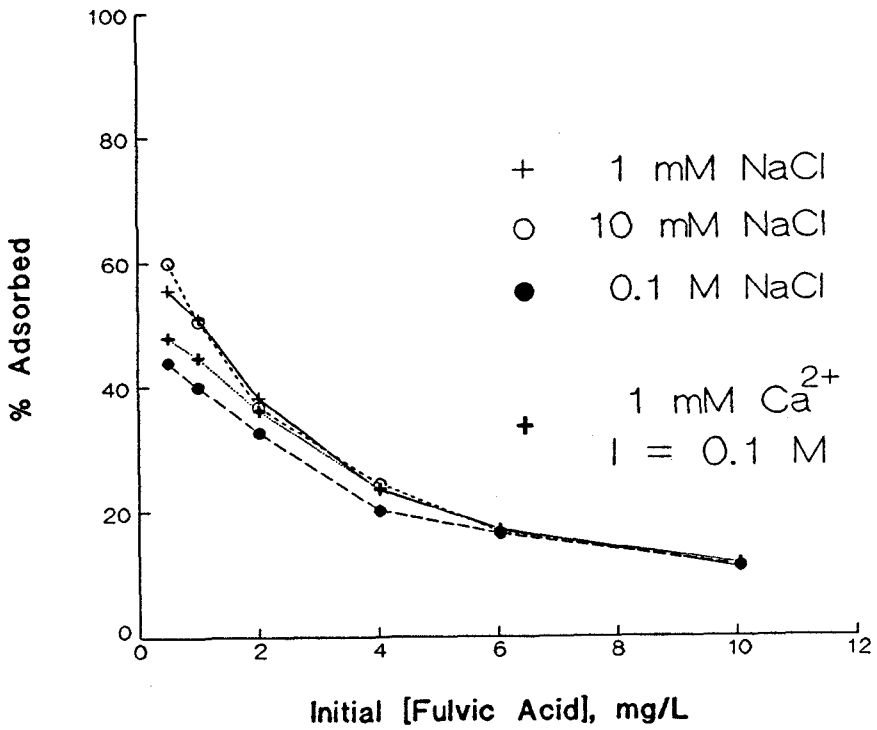


Figure 7. Fractional adsorption of fulvic acid on alumina at pH 4 versus initial fulvic acid concentration. Solid concentrations were 20 mg/L.

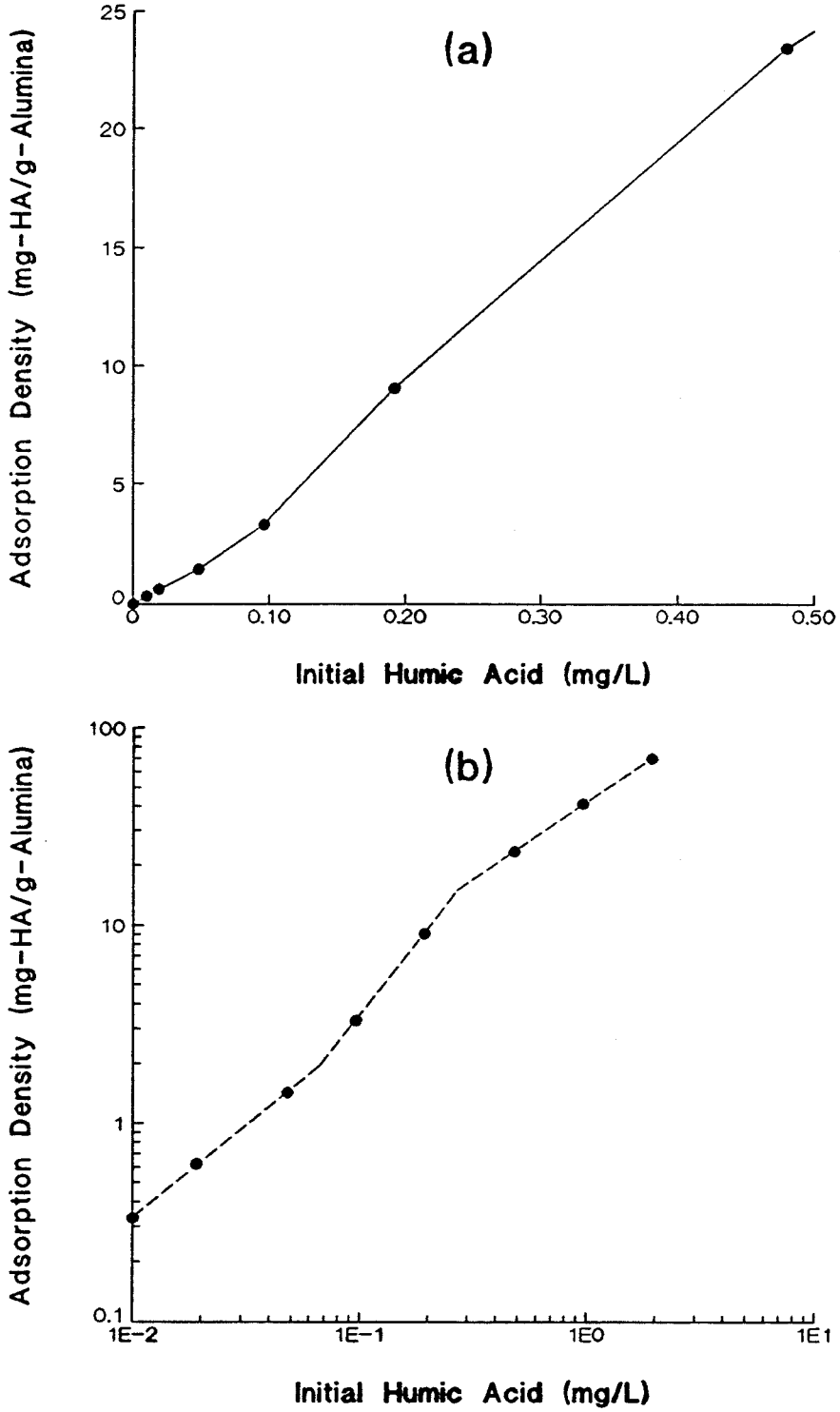


Figure 8. Adsorption of humic acid on alumina in 0.001 M NaCl at pH 4. Solid concentrations were 20 mg/L. a) Rectilinear plot exhibits S-shape at very low humic acid concentrations. b) Log-log plot shows the three distinct regions that generally characterize cooperative adsorption.

S-curve isotherms have been shown to occur as a result of cooperative interactions among adsorbed molecules (Giles, 1974a,b). These interactions cause the adsorbate to become stabilized on the surface, and they produce an enhanced affinity between the surface and adsorbate as the surface coverage increases. S-type isotherms are often observed in the adsorption of surfactants from solution and the mechanisms of adsorption in each region are relatively well-understood (Fuerstenau and Wakamatsu, 1975; Chandar et al., 1987; Holsen et al., 1991). In most cases of organic adsorption, the cooperative effects between adsorbate molecules result from hydrophobic interactions; for example, the interaction of each $-CH_2-$ group contributes ~RT to the total energy of adsorption for aliphatic organic compounds (Tanford, 1980; Israelachvili, 1985; Liang and Morgan, 1990a,b).

A useful way of comparing humic versus fulvic acid adsorption on alumina is to examine the relative amounts of carboxyl groups in the adsorbed layer at maximum adsorption. Although humic and fulvic acid have very different adsorption densities (Γ_m ~100 versus ~67 mg/g, respectively) and surface coverages (~100% versus ~33%) at saturation, they are expected to have relatively similar numbers of carboxyl groups bound if ligand exchange is the dominant adsorption mechanism for both organic materials.

The carboxyl group content of Suwannee River fulvic acid has been determined to be 6.1 mmol/g by potentiometric titration (Bowles et al., 1989) and 6.8 mmol/g by methylation and ^{1}H-NMR (Noyes and Leenheer, 1989); humic acid has 4.9 mmol/g of carboxyl groups as determined by potentiometric titration

(Thorn, 1989). Using these values and the data from Tables III and V, the carboxylate adsorption densities can be calculated at saturation for humic and fulvic acid. These values are listed in Table VI for the experiments conducted at pH 4.

At low NaCl concentrations, the number of carboxyl groups present in the adsorbed layer for humic acid is ~3.3 COO^-/nm^2. The majority of these carboxyl groups are most likely bound directly to the alumina surface via inner-sphere complexes because the concentration of NaCl is not expected to favor adsorption mechanisms other than ligand exchange. Significant hydrophobic bonding is not expected because the low electrolyte concentration would not effectively screen the large electrostatic repulsion which would exist if a substantial number of unbound carboxylate anions are present in the adsorbed layer.

The maximum amount of fulvic carboxyl groups present in the adsorbed layer at pH 4 is also ~3.3 COO^-/nm^2, and most of these carboxyl groups are also thought to be bound directly to the surface as inner-sphere complexes for reasons similar to those for humic acid. The relative insensitivity of fulvic carboxylate adsorption densities to the solution composition (Table VI) indicates that adsorption mechanisms other than ligand exchange are not operative for fulvic acid. At high electrolyte concentrations, hydrophobic bonding, if it were to occur, should be particularly enhanced for fulvic acid relative to humic acid because any electrostatic repulsion between unbound anionic groups would be smaller (fulvic acid only covers 1/3 of the surface at maximum adsorption).

Table VI. Carboxylate Adsorption Density.[a,b,c]

	Humic Acid	Fulvic Acid [d]
0.001 M NaCl	3.4	2.8 - 3.1
0.01 M NaCl	3.2	2.8 - 3.2
0.1 M NaCl	3.7	3.1 - 3.4
1 mM Ca^{2+} [e]	4.6	3.1 - 3.4

[a] Units of COO^-/nm^2.

[b] From maximum adsorption densities at pH 4.

[c] SA = 80 m^2/g.

[d] Values correspond to 6.1 and 6.8 mmol/g carboxyl groups.

[e] 0.1 M total ionic strength.

As the NaCl concentration is increased at pH 4, the humic carboxylate adsorption value increases to 3.7 COO^-/nm^2 (0.1 M NaCl solution); the presence of 1 mM Ca^{2+} at this same ionic strength further increases the amount adsorbed to 4.6 COO^-/nm^2. Assuming that a maximum of 3.3 COO^-/nm^2 can be bound as inner-sphere complexes, the additional carboxyl groups must then be held in the adsorbed layer by a hydrophobic-bonding mechanism. This mechanism becomes favored only when the electrostatic repulsion between unbound anionic groups becomes effectively screened as discussed previously (Sposito, 1984). Other possible adsorption mechanisms are not thought to be operative for these solution conditions; for example, 1 mM Ca^{2+} at pH 4 is not expected to enhance adsorption of humic substances by water bridging. Instead, the increase in adsorption in the presence of Ca^{2+} occurs because the bivalent cation is more effective than Na^+ in neutralizing the anionic charge in the adsorbed layer (Tipping, 1981; Davis, 1982).

The observed differences between humic and fulvic acid adsorption on aluminum oxide particles, therefore, appear to result from the presence of different adsorption mechanisms. For fulvic acid at pH 4, ligand exchange is the most important adsorption mechanism regardless of solution composition. The lack of enhanced adsorption at high ionic strength and, particularly, in the presence of Ca^{2+} indicates that most of the fulvic carboxyl groups are bound directly to the alumina surface via inner-sphere complexes and few unbound anionic groups are present in the adsorbed layer.

Ligand exchange is also thought to be a major adsorption mechanism for

humic acid for all solution compositions. However, other mechanisms may contribute to adsorption as the solution composition and humic acid concentration change. At pH 4 and 7, initial adsorption of humic acid at low organic material concentrations appears to be enhanced by cooperative effects between adsorbate molecules. At low NaCl concentrations, ligand exchange is the dominant adsorption mechanism at all pH values; cation bridging may be important at very high pH. As the NaCl concentration increases, hydrophobic bonding becomes more effective at pH 4 and 7 and cation bridging becomes increasingly important at pH 10. Adding Ca^{2+} ions to the solution has two major effects; at pH 10 it enables water bridging to occur and at all pH values it helps decrease electrostatic repulsion in the adsorbed layer.

The supposition that fulvic acid does not adsorb by hydrophobic bonding agrees with its relative solubility, polarity, and aromaticity relative to humic acid. Fulvic acid, by operational definition, is a relatively hydrophilic organic acid and remains soluble under all pH conditions. It is the dominant humic substance in natural waters (Thurman, 1985). Because fulvic acid contains fewer aromatic groups and is much more aliphatic than humic acid (Table I), its electronic polarizability is less than that for humic acid (Israelachvili, 1985). Therefore, it is not able to interact with a mineral surface through van der Waals interactions as effectively as humic acid. Because fulvic acid does not participate in hydrophobic bonding, its adsorption shows more dependence than humic acid on increases in pH (Figure 2). Hydrophobic bonding attenuates the decrease in adsorption by a ligand-exchange mechanism as the solution pH increases.

From the adsorption data presented, it appears that a maximum of ~3.3 carboxyl groups per nm^2 can be bound directly as inner-sphere complexes by the alumina surface. This value is much lower than 16.9 nm^{-2}, the site density of the aluminum oxide surface determined by fluoride adsorption/desorption (Table III). The carboxylate adsorption density is closer, however, to the site densities obtained by other researchers using saturation or (strictly) fluoride adsorption methods (Table IV). Also, it is in excellent agreement with the value of ~3.4 COO^-/nm^2 calculated using the maximum adsorption of benzoic acid observed on alumina by Kummert and Stumm (1980).

The discrepancy between the site density determined by fluoride adsorption/desorption and the observed carboxylate adsorption density most likely results from the fact that F^- is more electronegative than most carboxylate groups. Thus, more of the actual hydroxyl sites can be exchanged with fluoride ions as opposed to carboxylate ions. This brings up an interesting dilemma in the appropriate choice of a probe for determining experimental surface site densities (i.e., exchange capacities) of minerals. It would appear that exchange capacities should be operationally defined by use of appropriate probes whose characteristics are similar to the desired adsorbate(s). Therefore, it is conceivable that a properly characterized mineral might have more than one exchange capacity defined (e.g., capacities defined for H^+, COO^-, HPO_4^{2-} etc. exchange).

SUMMARY AND CONCLUSIONS

This study investigated the adsorption of Suwannee River humic substances on colloidal-sized aluminum oxide particles in order to elucidate how solution chemistry affects the formation and nature of organic surface coatings. It is postulated that the mechanisms by which humic material is adsorbed to minerals greatly influence the type of surface complex which is formed, and that different types of surface complexes will bind pollutant molecules dissimilarly. Because the different adsorption mechanisms are affected by the aqueous chemistry of natural waters, a systematic study of the effects of pH, ionic strength and background electrolyte composition on humic material adsorption was performed.

The amount of humic and fulvic acid adsorbed onto aluminum oxide particles decreased with increasing pH values for all solutions of constant ionic strength. In NaCl solutions at fixed pH values, the adsorption of humic material generally increased with increasing ionic strength; the increase was particularly notable at neutral to basic pH values. The presence of Ca^{2+} enhanced the adsorption of humic acid relative to NaCl solutions, and was especially significant at pH 10. Adsorption densities for both humic and fulvic acid showed good agreement with Langmuir isotherms. Qualitative interpretations of the adsorption processes were made utilizing the Langmuir isotherm parameters K_{ads} and Γ_m.

The adsorption density of humic acid on alumina was always observed to be higher than that of fulvic acid for identical solution conditions. The increased adsorption of humic acid relative to fulvic acid agreed with predictions from

correlations based on aromaticity, molecular weight and polarity. Other differences in the adsorption of humic and fulvic acid were: (1) the adsorption of fulvic acid showed more dependence on pH than did humic acid; (2) the affinity of alumina for humic acid was much larger than for fulvic for identical solution conditions; and (3) the presence of Ca^{2+} at pH 4 enhanced the adsorption of humic acid but had little effect on fulvic acid adsorption.

The observed differences between humic and fulvic acid adsorption on alumina appeared to result from the presence of different adsorption mechanisms. For fulvic acid, ligand exchange was the most important adsorption mechanism regardless of solution composition. Although ligand exchange was also a major adsorption mechanism for humic acid, other mechanisms contributed as the solution composition and humic acid concentration changed. At pH 4 and 7, adsorption of humic acid at low initial concentrations was enhanced by cooperative effects between adsorbate molecules. As the NaCl concentration increased, hydrophobic bonding became more effective for humic acid at pH 4 and 7 while Na^{+} bridging became increasingly important at pH 10. Adding Ca^{2+} ions to the solution had two major effects: at pH 10 it enabled water bridging to occur and at all pH values it helped decrease electrostatic repulsion in the adsorbed layer.

Carboxyl group densities in the adsorbed layer were calculated for humic and fulvic acid at maximum adsorption. From the adsorption data, it appears that a maximum of 3.3 carboxyl groups per nm^2 are bound directly as inner-sphere complexes by the surface of the aluminum oxide particles used here. This value is in

good agreement with experimental site densities determined by other researchers using saturation and fluoride adsorption techniques and agrees very well with a previously determined maximum adsorption density for benzoic acid.

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Chapter 4

BINDING OF A FLUORESCENT HYDROPHOBIC ORGANIC PROBE BY DISSOLVED HUMIC SUBSTANCES AND ORGANICALLY-COATED ALUMINUM OXIDE SURFACES

ABSTRACT

The binding of perylene by Suwannee River humic substances in the presence and absence of colloidal-sized aluminum oxide particles was examined using a fluorescence quenching technique. The fluorescence of perylene associated with dissolved and adsorbed humic substances appeared to be fully quenched as evidenced by quantum yields which approached zero for all complexes. Binding of perylene by the humic material was complete within 3 minutes after spiking the samples with the hydrophobic probe. In the absence of alumina, both humic and fulvic acid were able to bind perylene and the partition coefficients varied inversely with pH and NaCl concentrations. The presence of Ca^{2+} had little effect on the binding of perylene by either of the dissolved humic substances. The adsorption of humic and fulvic acid onto alumina decreased their ability to bind perylene. For all solution conditions examined, association of perylene with adsorbed fulvic acid was never detected. In NaCl solutions, partition coefficients for adsorbed humic acid at low pH were approximately half the values of those for dissolved humic acid; at neutral to high pH, alumina-bound humic acid did not bind perylene in NaCl solutions. In contrast to the results observed for dissolved humic acid, the presence of Ca^{2+} greatly enhanced the binding of perylene by adsorbed humic acid. A major effect of solution chemistry is to alter the mechanisms by which humic substances adsorb to alumina, and different adsorption mechanisms determine how tightly organic material is bound to the surface. The ability of weakly-adsorbed humic acid to bind perylene, and possibly many of its other properties, approaches that of the dissolved species.

INTRODUCTION

The geochemistry, and ultimately the fate, of organic compounds is strongly dependent on chemical reactions that occur at the solid-liquid interface of particles. These reactions can greatly affect the mobility, bioavailability, reactivity and toxicity of organic compounds. The partitioning of nonionic hydrophobic organic compounds (HOC) in surface soils and sediments has been shown to depend primarily on the hydrophobicity of the compound and the fraction of organic carbon (f_{oc}) in the sorbent (Karickhoff et al., 1979; Means et al., 1980; Chiou et al., 1979, 1981). The importance of the organic carbon content of sediments and soils suggests that various components of natural organic material (NOM) bind nonionic HOC in solution and at mineral surfaces.

Partitioning of HOC between NOM and water has been modeled analogously to the dissolution of the compound in an organic solvent; in this case, the NOM forms a "microscopic organic phase." The mechanism of partitioning results from the "hydrophobic interaction," a combination of relatively small van der Waals bonding forces and a substantial thermodynamic gradient which drives the organic molecules out of aqueous solution (Voice and Weber, 1983). The van der Waals attraction forces between organic molecules are generally dominated by London dispersion forces (induced dipole-induced dipole) with smaller or no contributions from Keesom orientation forces (dipole-dipole) and Debye induction forces (dipole-induced dipole). The thermodynamic driving force is the increase in entropy upon breakdown of the highly-structured coordination shell of water molecules surrounding the

hydrophobic solute. The hydrophobic interaction has been discussed in detail by Tanford (1980) and Israelachvili (1985).

Recently, much work has been focused on studying the binding of hydrophobic pollutants by dissolved organic material (DOM) in solution (e.g., Carter and Suffet, 1982; McCarthy and Jiminez, 1985; Chiou et al., 1986, 1987; Garbini and Lion, 1985, 1986; Gauthier et al., 1986, 1987; Traina et al., 1989; Backhus and Gschwend, 1990). Collective results from these studies suggest that the binding of hydrophobic organic pollutants by DOM depends on the chemical and structural characteristics (i.e., the "quality") of the DOM and may depend on the aqueous chemistry of the system.

In the environment, organic material adsorbs at particle surfaces and can dominate the properties of the solid-liquid interface. While only a fraction of the NOM in aquatic systems may be adsorbed on particle surfaces, the solid surface may be entirely covered by organic material and thus exhibit the physical and chemical properties of the organic matter. In effect, the adsorbed species may be thought of as an organic "film" coating particle surfaces. These organic surface coatings modify particle-pollutant interactions which occur at the solid-liquid interface or on particle surfaces. Because stabilization of particles by NOM is a common observation, the transport and fate of NOM, particles and particle-reactive compounds in natural waters are complex, interdependent processes.

Very few studies have investigated the association of HOC with mineral-bound NOM. Backhus and Gschwend (1990) examined groundwater samples from three

different monitoring wells in order to determine the in situ organic material's ability to bind polycyclic aromatic hydrocarbons (PAHs). They spiked both whole and ultrafiltered (500 molecular weight cutoff) samples with PAH probes. The unaltered, whole samples were believed to contain organic colloids and/or inorganic colloids with organic coatings. Analysis and characterization of the organic material in solution versus that on particle surfaces were not made, nor was the fractional binding of perylene between dissolved and adsorbed organic material determined.

Garbini and Lion (1985) used an equilibrium headspace technique to examine the binding of the relatively volatile compounds trichloroethylene and toluene by a commercial humic acid and by alumina particles coated with the same humic acid. They observed that association of the solutes with dissolved humic acid was nearly three times as much as that with humic acid adsorbed on alumina, suggesting that the sorptive capacity of humic acid was reduced by the presence of a hydrous oxide surface. They hypothesized that the observed reduction was because of differences in the physical and/or chemical nature of free versus adsorbed humic acid, selective adsorption of a certain fraction of humic acid to the alumina surface, and/or pH differences in aqueous phases containing the respective sorbents (i.e., pH was not controlled in their experiments).

Murphy et al. (1990) examined the sorption of carbazole, dibenzothiophene and anthracene onto hematite and kaolinite which had been coated with natural humic substances. Because the observed sorption isotherms were nonlinear, they hypothesized that adsorption onto rather than partitioning into the surface organic

phase was the sorption mechanism. Anthracene, the most hydrophobic compound, showed the greatest binding while the humic substance with the highest aromaticity, peat humic acid, was the strongest sorbent. The particular mineral used influenced the amount of binding observed; however, because binding measurements were not made in the absence of minerals, the effect of mineral surfaces on the ability of humic substances to bind hydrophobic organic compounds could not be determined.

This study investigated the ability of adsorbed humic substances to bind nonpolar HOC relative to "freely dissolved" humic material. A principal hypothesis was that the conformation and polarity of humic substances play important roles in their adsorption onto mineral surfaces and in their ability to bind hydrophobic pollutants both in solution and at the solid-liquid interface. Because the conformation and polarity of humic materials and the mechanisms of their adsorption onto mineral surfaces are affected by the aqueous chemistry of natural waters, a systematic study of the effects of pH, ionic strength and the presence of bivalent cations was undertaken. The objectives of this study, therefore, were to (1) determine the amount of binding of a hydrophobic organic probe by dissolved (i.e., not adsorbed) humic material, (2) quantify the amount of binding of the probe by adsorbed humic substances, and (3) investigate the effects of different adsorption mechanisms on the ability of adsorbed humic substances to bind the probe.

Several methods have been used previously to study the partitioning of HOC between NOM and water, including dialysis, reverse phase separation, ultrafiltration and centrifugation. These methods rely on the separation of NOM from the aqueous

phase to quantify the amount of pollutant associated with organic material. The inability to completely separate NOM from water has resulted in observations of a "solids effect" in some studies (Carter and Suffet, 1982; Landrum et al., 1984; Gauthier et al., 1986; Murphy et al., 1990), in which the measured carbon-normalized partition coefficient decreases with increasing concentrations of organic carbon. In studies which used techniques that did not require a separation (e.g., headspace analysis and fluorescence quenching), a solids effect was not observed (Garbini and Lion, 1985; Gauthier et al., 1986, 1987). Problems with separating NOM from water have been recognized previously as the cause for observed solids effects (Gschwend and Wu, 1985; Morel and Gschwend, 1987; Voice et al., 1983; Voice and Weber, 1985). Therefore, methods capable of measuring the concentrations in situ are ideal because separation difficulties may introduce artifacts in the determination of partition coefficients.

An important objective of this study was to distinguish between association of the hydrophobic probe with humic substances in solution versus humic material adsorbed on the aluminum oxide surface. This was necessary in order to avoid a separation and resuspension of adsorbed humic material before a partitioning experiment. There was concern that separation of the humic substances adsorbed to the alumina surface from that remaining in solution would disrupt equilibria and lead to variable estimates of binding constants, much like that observed upon separating pollutants equilibrated between two phases (Gauthier et al., 1986).

In order to elucidate the effects of aqueous chemistry apart from the effects of the quality of natural organic material (e.g., Gauthier et al., 1987; Garbini and Lion, 1986; Chiou et al., 1986), well-characterized humic materials were chosen as models to represent NOM. Aquatic humic substances constitute 40 to 60 percent of the dissolved organic carbon, and are the largest fraction of NOM, in water (Thurman, 1985).

Commercially-available colloidal-sized aluminum oxide particles (Aluminum Oxide C) were used in this study as a model for mineral surfaces. These small (26 nm) particles have high specific surface areas and can form relatively stable particle suspensions. Alumina has a relatively high zero point of charge (pH_{zpc} ~8.5), and thus is a good sorbent for organic acids. Because Aluminum Oxide C has been used for adsorption studies by previous researchers (e.g., Kummert and Stumm, 1980; Bales, 1984; Davies, 1985; Schultess and Sparks, 1987), its surface characteristics are relatively well-known.

Perylene was the fluorescent probe chosen to model hydrophobic organic pollutants. This nonpolar, nonionogenic PAH compound was selected in order to eliminate or minimize possible adsorption mechanisms other than the effect of hydrophobic interactions in the binding reaction. PAHs have been used previously as models for nonionic HOC (e.g., Karickhoff et al., 1979; Landrum et al., 1984; Whitehouse, 1985; McCarthy and Jiminez, 1985; Gauthier et al., 1986, 1987; Traina et al., 1989; Backhus and Gschwend, 1990). PAH compounds fluoresce in

aqueous solution, but the fluorescence is quenched when they are associated with NOM. Thus, the fraction of perylene associated with NOM can be determined without separating the NOM from the aqueous phase.

EXPERIMENTAL

Apparatus. Fluorescence measurements were made on a Shimadzu Model RF-540 Recording Spectrofluorophotometer with a right angle geometric sample chamber configuration. The excitation source was a 150W xenon-arc lamp and excitation and emission wavelengths were obtained with off-plane concave diffraction grating (900 lines/mm) monochromators. Fluorescence measurements for perylene and rhodamine 110 were made at the excitation/emission wavelengths of 432/470 and 496/520 nm, respectively, with slits set for bandwidths of 10 nm on both the excitation and emission monochromators.

Absorbance measurements were made on a Hewlett Packard 8451A Diode Array Spectrophotometer at the appropriate wavelengths to correct for the inner-filter effect. The spectral bandwidth was fixed at 2 nm. The spectrophotometer was equipped with a Hewlett Packard 89055A cell stirring module to allow mixing in the cells.

Fused silica fluorescence cells (Spectrosil, Starna Cells Inc.) with Teflon stoppers were used for both fluorescence and absorbance measurements. Fused silica cells contribute very little background fluorescence relative to quartz cells and are generally recommended for fluorescence work. The cells had a path length of 10 mm.

The pH of all aqueous solutions was measured with a Radiometer Model PHM84 Research pH Meter using a Radiometer GK2401C glass combination electrode. The pH meter was calibrated with NBS buffers.

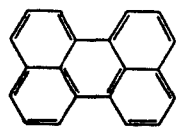
Materials. (A) General. All reagents not specifically referred to were of analytical grade or better and were used without further treatment. All aqueous stock solutions were filtered through 0.2 μm pore polycarbonate Nuclepore filters.

(B) Fluorescent Probes. The hydrophobic probe used in this study was perylene (Aldrich, 99+% pure). Relevant chemical and physical properties of perylene are listed in Table I. The conservative probe, rhodamine 110 (Lasergrade), was obtained from Kodak. Both were used without further purification.

A concentrated stock solution of rhodamine 110 (2.7 g/L, 7.4 mM) was prepared in methanol (Fisher, Spectroanalyzed). Because of its relatively low solubility in methanol, perylene was first dissolved in chloroform (J.T. Baker, Photrex) and an aliquot of this solution (120 mg/L, 475.6 μM) was then spiked into methanol to obtain the desired stock concentration. Finally, an aliquot of the concentrated stock of rhodamine 110 was spiked into the perylene stock to obtain the final working stock solution (120 μg/L (475.6 nM) perylene, 30 μg/L (81.8 nM) rhodamine 110 in methanol with 0.1% (v/v) chloroform). This solution was stored in the dark at 4°C in an amber borosilicate glass bottle to prevent photodegradation and/or volatilization. Aliquots of the solution were allowed to equilibrate (in the dark) at room temperature for at least 24 hours before use in the experiments.

(C) Humic Substances. Well-characterized humic materials were obtained from the International Humic Substances Society (IHSS) and used without further purification. Suwannee River standard humic acid and Suwannee River standard fulvic acid were isolated from the Suwannee River which drains the Okefenokee

Table I. Chemical and Physical Properties of Perylene.

Structure	
Formula	$C_{20}H_{12}$
FW (g/mol)	252.32
Solid Density (g/cm^3)	1.35
mp (°C)[a]	277-279
ϕ_F [b]	~1.0
Molecular Length [c] (Å)	10.5
Total Surface Area [d] ($Å^2$)	251.5
Molar Volume [e] (mL)	202
log K_{ow} (M/M) [d]	6.50
distilled water solubility [f] (μg/L)	0.4
(nM)	1.585
γ_i^w [g]	(x 10^{-7})
Distilled Water	8.721
0.001 M NaCl	8.727
0.01 M NaCl	8.793
0.1 M NaCl	9.461

[a]Supplied by Aldrich. [b]Quantum yield in aqueous solution [25°C] (Turro, 1978). [c]Estimated for major-axis from data of Klevins (1950). [d]Yalkowsky and Valvani (1979). [e]Estimated from correlation with solid density using data of Davis and Gottlieb (1962). [f]MacKay and Shiu (1977). [g]Calculated in Chapter 2.

Swamp in southern Georgia. Isolation procedures and characterization of these materials have been reported (Averett et al., 1989). Chemical properties of the humic and fulvic acids are shown in Table II and some physical properties are listed in Table III.

Because the humic materials received are very hygroscopic, they were stored in a desiccator until needed. Concentrated stock solutions were prepared by dissolving weighed amounts of the humic material in deionized, distilled water (D_2H_2O). The solutions were mixed and allowed to stand in the dark for at least 24 hours. The humic stock solutions were filtered through prewashed 0.2 μm pore polycarbonate Nuclepore filters to remove possible particle contamination and were then stored in amber borosilicate glass bottles similarly to the perylene solution.

Absorbance spectra and measurements at the wavelength of 250 nm were taken of the humic and fulvic acid stock solutions before and after filtering to check for possible loss and/or fractionation of material. No such effects were observed.

(D) Alumina. The hydrous oxide particles used in this study were γ-Al_2O_3 (Degussa, Aluminum Oxide C). Aluminum Oxide C is produced by flame hydrolysis of anhydrous aluminum chloride and Debye-Scherrer x-ray diffraction patterns reveal that it has primarily a gamma structure with a slight delta structure. The chemical purity is >99.6% and the density is 2.9 g/cm^3. Pretreatment and preparation of stock particle suspensions have been reported in Chapter 3. The average particle diameter from TEM was 26 nm with a range observed from 14-50 nm. Additional data for the aluminum oxide particles are listed in Table IV.

Table II. Chemical Properties of IHSS Standard Suwannee River Humic Substances.

Elemental Analysis (%) [a] and Atomic Ratios [b]

(Ash-Free and Moisture-Free Basis)

	C	H	O	N	S	P	Total	Ash	O/C [b]	H/C [b]	C/N [b]
Humic Acid	54.22	4.14	39.00	1.21	0.82	0.01	99.40	3.19	0.54	0.91	52.25
Fulvic Acid	53.75	4.29	40.48	0.68	0.50	0.01	99.71	0.82	0.57	0.95	92.18

[a] Supplied by International Humic Substances Society (IHSS).

[b] Calculated from elemental analysis.

Structural Carbon Distributions [a]

(% of Total Carbon)

	Ketone-C (220-180)	Carboxyl/ Carbonyl-C (180-160)	Aromatic-C (160-105)	Aromatic/ Acetal-C (105-90)	Aliphatic -HCO (90-60)	Aliphatic -CH (60-0)	sp^2 (220-90)	sp^3 (90-0)	Aromaticity f_a [b]
Humic Acid	7	16	42	6	12	17	71	29	0.42
Fulvic Acid	6	19	28	5	15	27	58	42	0.28
group density [c] (g/mL)	1.74	1.878	1.601	1.601	1.620	0.72			

[a] Determined from liquid-state ^{13}C NMR [ppm range shown in parentheses] (Thorn, 1989).

[b] f_a = spectrum area from 160-105 ppm divided by total spectrum area.

[c] Group density contribution to calculated density (Brown and Leenheer, 1989).

Table III. Physical Properties of IHSS Standard Suwannee River Humic Substances.

	Humic Acid	Fulvic Acid
Radius of Gyration (Å) [a]		
pH 6	11.1	7.2
pH 9	11.4	7.7
M_n (daltons)	1100 [a]	800 [b]
Density (g/mL) [c]	1.508	1.427
v_{app} (mL/g)	0.6631	0.7008
V_p (mL/mole) [d]	730	560

[a] Determined by small-angle X-ray scattering (Aiken et al., 1989).

[b] Determined by vapor-pressure osmometry (Aiken et al., 1989).

[c] Calculated from structural carbon distributions (Table III).

[d] $M_n \div$ Density.

Table IV. Surface Properties of Aluminum Oxide.[a]

Formula		γ-Al_2O_3	
Specific Surface Area (m^2/g) (EGME Retention)		80	
Exchange Capacity (mmoles/g) (Fluoride Adsorption/Desorption)		2.24	
Site Density (nm^{-2})		16.9	
Surface Acidity Constants			
Model	Diffuse Layer	Stern Layer	
C_1 (F/m^2)	---	6.0	5.4
pK_1^s	6.8	7.7	8.2
pK_2^s	10.0	9.3	8.8
pH_{zpc}	8.4	8.5	8.5

[a] Data from Chapter 3.

Procedure. (A) General. Unless specified otherwise, all experiments were performed at room temperature (23° C) in an open system (i.e., aqueous solutions were equilibrated with the surrounding atmosphere). The open system is a model which approximates the carbonate system of natural waters by equilibrating water with the atmosphere containing $CO_{2\,(g)}$ at a constant partial pressure (Stumm and Morgan, 1981). For waters which are in equilibrium with the atmosphere, the huge reservoir of $CO_{2\,(g)}$ imparts a significant buffering action above pH 7.

Aqueous solutions were prepared with distilled, deionized water (D_2H_2O) (Corning Mega-Pure™ System). Polycarbonate filters (Nuclepore, Pleasanton, CA) with pore sizes of 15 or 50 nm were used for all aluminum oxide particle separations.

Fluorescence cells were cleaned by repeated soaking and rinsing, first with methanol and then D_2H_2O. Cell cleanliness was monitored with fluorescence and absorbance measurements. All other glassware was cleaned by soaking in either 4 M HNO_3 or 4 M HCl, rinsing repeatedly with D_2H_2O, and drying in an oven at 110° C.

Absorbance spectra were taken to determine the possible wavelengths which could be used for excitation of perylene and rhodamine 110. Fluorescence emission spectra were obtained by exciting the compounds at the wavelength of an absorption band in order to determine wavelengths at which fluorescence could be observed. The fluorescence emission spectrum of a pure substance is independent of the wavelength of excitation (Parker, 1968). Finally, fluorescence excitation spectra were recorded and an appropriate pair of excitation/emission wavelengths were selected

for each compound. Wavelength pairs were chosen to maximize the fluorescence intensity and minimize the background interference (e.g., from quencher fluorescence and/or the Raman scattering of water).

(B) Adsorption of Humic Substances. Adsorption isotherms of humic and fulvic acid on alumina were obtained at constant pH and ionic strength values. Very low solids concentrations (~20 mg/L) were used in order to maximize the adsorption density (i.e., obtain high surface coverages) and minimize the effects of particle coagulation in the adsorption experiments and, particularly, in the subsequent partitioning experiments.

Sample solutions were prepared by adding appropriate amounts of concentrated salt solution(s) and varying amounts of humic material stock solutions to D_2H_2O in Erlenmeyer flasks and adjusting the pH with 0.1 M HCl and/or 0.1 M NaOH. The samples were stirred until no further pH change was observed, indicating that they had reached equilibrium with the atmosphere. Aliquots of the working alumina suspension were then added to obtain the proper (calculated) solids concentration, and the pH was adjusted if necessary. The samples were then removed from the stirrer and the flasks were covered with parafilm and stored in the dark. The samples were not mixed during the adsorption period in order to avoid coagulation of the particles.

After a 24-hour adsorption period, the pH of each sample was checked and a 3-mL aliquot was removed for the partitioning experiment. The remaining portion of each sample was analyzed to determine the quantity of humic material adsorbed

on the aluminum oxide particles. Organic carbon concentrations were measured with a Shimadzu Model TOC-500 total organic carbon analyzer.

Humic material blanks (no alumina) were prepared at the same DOM concentrations as the adsorption samples and were used in the partitioning experiment. The humic blanks and sample aliquots removed for the partitioning experiment were usually used immediately and always within one day to minimize the effects of hydrolysis of the acids (Bowles et al.,1989).

(C) Partitioning of Perylene. The fluorescence quenching method used for perylene was adapted from Backhus and Gschwend (1990). A typical experiment consisted of pipetting 3 mL of a sample of known pH, ionic strength and total humic/fulvic acid concentration (either free in solution, adsorbed onto alumina or a combination of the two) into a fluorescence cell containing a micro stir bar and recording the absorbance and fluorescence intensities at the excitation/emission wavelengths for perylene and rhodamine 110. These values reflect the background intensities of solution components. The sample was then spiked with 10 μL of the combined perylene-rhodamine 110 stock solution and was immediately placed in the stirring module of the spectrophotometer. While mixing, the lid to the sample compartment was closed to prevent photodegradation.

After 3 minutes, the cell was placed in the spectrofluorophotometer and a fluorescence measurement for perylene was made. The sample was then returned to the spectrophotometer for an absorbance measurement and further mixing. This procedure was repeated for a total elapsed time of 40 minutes. When the rate of

change of perylene fluorescence intensity decreased sufficiently (after 20 minutes), fluorescence measurements were made for rhodamine 110 as well.

The initial perylene concentration of the samples after spiking was nominally 0.4 μg/L (1.6 nM) while the rhodamine 110 concentration was nominally 0.1 μg/L (0.27 nM). In order to account for the slight variation in spiking volume between the different samples, the corrected perylene fluorescence intensities were normalized by the mean of the corrected rhodamine 110 fluorescence intensities.

Data Treatment. (A) Adsorption of Perylene to Glassware. For very hydrophobic PAH probes which sorb appreciably to inorganic surfaces, adsorption of the probe to fluorescence cell walls greatly decreases the solute concentration in aqueous solution. The observed decreases in fluorescence intensities are then not only caused by NOM static fluorescence quenching, but also by the adsorption of the PAH to glassware (i.e., a removal of the probe from solution). Backhus and Gschwend (1990) derived the following equation to describe observed fluorescence versus time by assuming that a first-order reaction described the PAH sorption to glassware:

$$F = \frac{k_{-w} F_0^*}{k_w + k_{-w}} + \frac{k_w F_0^*}{k_w + k_{-w}} \exp[-(k_w + k_{-w})t] \qquad (4.1)$$

where F_0^* = $[PAH_T]$ - [PAH-OC] at time zero and k_w and k_{-w} are the first-order forward and reverse rate constants for wall adsorption. $[PAH_T]$ and [PAH-OC] are the total PAH concentration and the mass of PAH bound by NOM per unit volume

of sample, respectively. By fitting equation (4.1) to experimental data and back-extrapolating to t = 0, they obtained the hypothetical fluorescence values which would have been observed had the PAH not been adsorbing to glassware.

(B) Binding of Perylene by Dissolved Humic Substances. Most analyses using fluorescence quenching techniques to determine partition coefficients rely on the assumption that only the free PAH solute contributes to the observed fluorescence. The assumption is valid only if the fluorescence of the PAH associated with NOM is totally quenched (i.e., that the fluorescence quantum yield of the PAH-NOM complex, ϕ, is zero). However, for different types of NOM, or as chemical conditions of the system change, this assumption may not be valid and must be verified.

Backhus and Gschwend (1990) showed that if the fluorescence of a PAH probe associated with one type of NOM (e.g., dissolved humic material in this study) is not totally quenched, than the observed fluorescence of the probe is described by:

$$F \propto [PAH_T]\,(\textit{fraction dissolved} + \phi(\textit{fraction bound})) \tag{4.2}$$

The fractions of the PAH probe in solution and associated with dissolved humic substances are given by the following two expressions:

$$\textit{fraction dissolved} = \frac{[PAH_d]}{[PAH_T]} = \frac{1}{1 + K_{oc}[OC]} \tag{4.3}$$

$$\textit{fraction bound} = \frac{[PAH\text{-}OC]}{[PAH_T]} = \frac{K_{oc}[OC]}{1 + K_{oc}[OC]} \tag{4.4}$$

where $[PAH_d]$ is the dissolved PAH concentration, K_{oc} is the partition coefficient normalized to carbon, and [OC] is the organic carbon concentration of the dissolved humic material. By combining the above equations, Backhus and Gschwend (1990) showed that the fluorescence ratio may be written as a function of [OC]:

$$\frac{F}{[PAH_T]} \propto \frac{F}{F_0} = \frac{1 + \phi K_{oc}[OC]}{1 + K_{oc}[OC]} \tag{4.5}$$

With this formulation, as [OC] $\Rightarrow \infty$, the normalized fluorescence asymptotically approaches ϕ. The K_{oc} can be obtained from the curve as the value of $[OC]^{-1}$ at the point where $F/F_0 = (1 + \phi)/2$.

(C) Binding of Perylene By Dissolved and Adsorbed Humic Substances. In natural waters, NOM adsorbs at mineral surfaces; thus, a second "compartment" of organic material which may bind the PAH probe is now considered to be present in the system. In this study, the second compartment of NOM is humic material adsorbed at and coating the aluminum oxide surface. In the presence of dissolved and adsorbed humic substances, the fluorescence intensity of the PAH probe may now be described by:

$$F \propto [PAH_T] \begin{pmatrix} \textit{fraction dissolved} \\ + \phi\,(\textit{fraction bound-free Hu}) \\ + \phi_B(\textit{fraction bound-adsorbed Hu}) \end{pmatrix} \tag{4.6}$$

where the extra term relative to equation (4.2) represents the probe associated with the organic coating on alumina particles. The fractions of the PAH probe in solution,

associated with dissolved humic material, and associated with humic material adsorbed at the aluminum oxide surfaces are given by:

$$\textit{fraction dissolved} = \frac{1}{1 + K_{oc}[OC] + K_{oc}^{B}[OC]_{B}} \tag{4.7}$$

$$\textit{fraction bound-free Hu} = \frac{K_{oc}[OC]}{1 + K_{oc}[OC] + K_{oc}^{B}[OC]_{B}} \tag{4.8}$$

$$\textit{fraction bound-adsorbed Hu} = \frac{K_{oc}^{B}[OC]_{B}}{1 + K_{oc}[OC] + K_{oc}^{B}[OC]_{B}} \tag{4.9}$$

where the superscript and subscript "B" signifies adsorbed humic material. Combining the above equations gives an expression describing the fluorescence ratios analogous to that derived by Backhus and Gschwend (1990):

$$\frac{F}{[PAH_T]} \propto \frac{F}{F_0} = \frac{1 + \phi K_{oc}[OC] + \phi_B K_{oc}^{B}[OC]_{B}}{1 + K_{oc}[OC] + K_{oc}^{B}[OC]_{B}} \tag{4.10}$$

The normalized fluorescence intensity is now observed to be a function of two variables, [OC] and $[OC]_B$. In applying equation (4.10) to experimental data, the values of ϕ and K_{oc} were obtained from prior experiments without aluminum oxide particles present (i.e., humic material blank solutions or "homogeneous" solutions). Utilizing these previously determined values, the values for ϕ_B and K_{oc}^{B} were determined for systems having both dissolved and adsorbed humic material present.

RESULTS AND DISCUSSION

Fluorescence Quenching for Unstable Particle Suspensions. The fluorescence quenching method used in this study to monitor perylene concentrations was adapted from Backhus and Gschwend (1990). Because the background fluorescence intensity from solution components was determined for each sample prior to spiking with perylene, the method was intended for use with stable colloid sample suspensions.

However, for a few samples containing the organically-coated aluminum oxide particles it was noted that coagulation and sedimentation of the particles were probably occurring in the fluorescence cells during the course of the quenching portion of the experiment. This hypothesis was based on the following observations:

(1) The corrected fluorescence intensities of the samples at time zero [obtained from equation (4.1)] were higher than expected and were sometimes even higher than the corrected fluorescence intensity of the blank sample.

(2) The values of the first-order forward rate constants for loss of perylene to wall adsorption [k_w in equation (4.1)] were abnormally high relative to other samples.

(3) The net fluorescence intensities for the conservative dye rhodamine 110 decreased systematically over the time period of 20 to 40 minutes (the time period for which the fluorescence was measured for rhodamine 110).

These anomalies were observed because the background fluorescence values, measured before spiking the samples with perylene, were assumed to remain constant for the 40-minute period.

Upon checking the absorbance values (used for the inner-filter corrections) of these particular samples, an "exponential-type" decay in absorbance versus time was observed (Figure 1b). For all of the "stable" particle suspensions, as well as the samples without aluminum oxide particles present (i.e., those containing only dissolved humic substances or blanks), the absorbance values were scattered around a constant value (Figure 1a,c). Because absorbance does not detect the low concentrations of perylene and rhodamine 110 in the samples (Chapter 2), the values only reflect the sample solution components (e.g., NOM and particle concentrations).

The sample suspensions which were observed to be coagulating and settling all had a low amount of NOM in the system. It appeared that the adsorbed humic substances moved the particles in these suspensions close to the region where they had a low stability, and further increases in NOM restabilized the particles (Figure 1) as Liang and Morgan (1990a,b) had observed for submicron hematite particles. Upon particle sedimentation, the background fluorescence (most of which resulted from scattering due to particles) decreased for both perylene and rhodamine 110. By using the initial background fluorescence intensities to correct all data, the artifacts observed above [(1) and (2)] were introduced.

The apparent exponential decrease in absorbance versus time most likely resulted from sedimentation and removal of the particles from the path of fluorescence detection. To a first approximation, the rate of sedimentation can be modeled from (Stumm and Morgan, 1981):

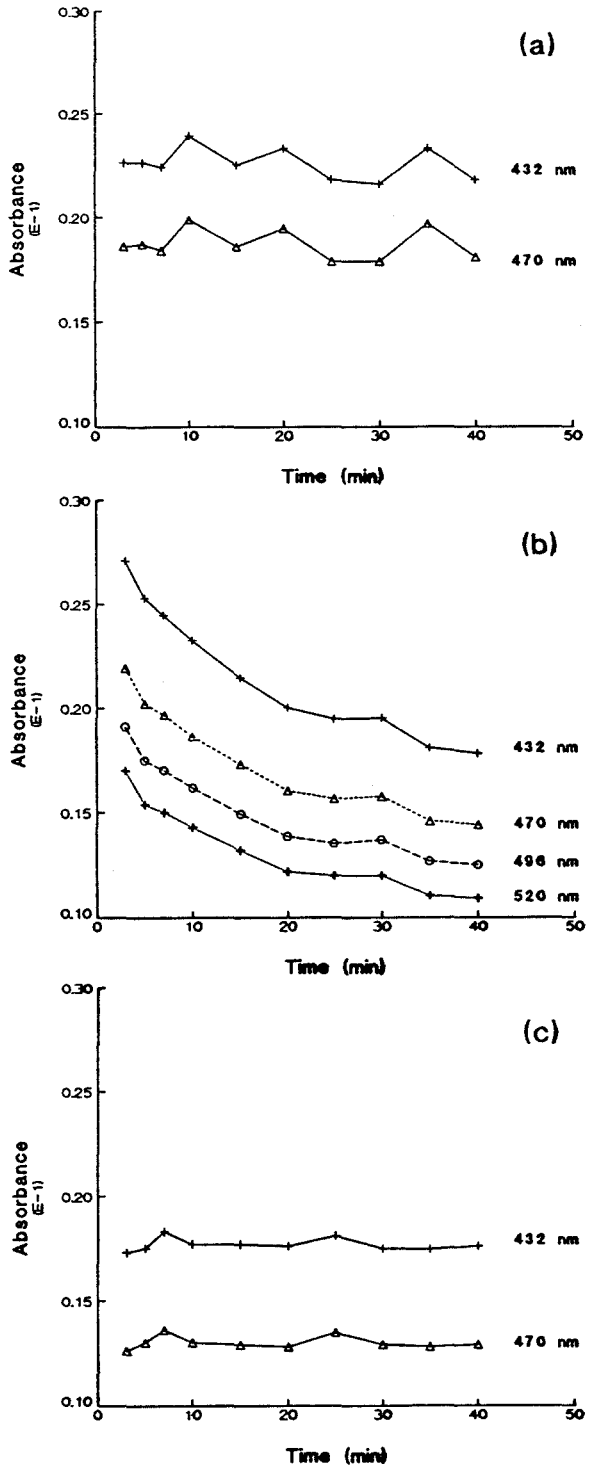


Figure 1. Absorbance as a function of time for suspensions of aluminum oxide particles with varying total concentrations of humic acid in 0.001 M NaCl at pH 4. The alumina solid concentrations were 20 mg/L. a) 0.43 mg/L humic acid. b) 0.86 mg/L humic acid. c) 1.72 mg/L humic acid.

$$\frac{dM}{dt} = J_{in} - J_{out} \tag{4.11}$$

where M is the mass of aluminum oxide particles in the system and J_{in} and J_{out} are the input and removal fluxes, respectively, of the particles. For systems with no material added, the input flux is zero. Assuming the removal rate is proportional to the total amount of material present, that is, J_{out} = kM, where k is the rate constant for the removal of material from the system, equation (4.11) may be written:

$$\frac{dM}{dt} = -kM \tag{4.12}$$

Solving equation (4.12), and assuming the observed absorbance and fluorescence intensities are proportional to the particle mass present, gives:

$$\frac{A}{A_0} = \frac{F}{F_0} = e^{-kt} \tag{4.13}$$

where A and F denote the absorbance and fluorescence intensities, respectively. The validity of the assumption that A, F $\propto$ M can be observed in Figure 1b. Since the four absorbance data sets are tracking the same process, the curves are, and should be, parallel with the same decay time constant. The fluorescence decay curves will likewise have the same decay time constant.

The approach used to correct the background fluorescence intensities for the unstable sample particle suspensions was to (1) fit exponential decay curves to the absorbance data for the four different wavelengths, (2) use the average values from these fits to generate new background fluorescence intensities (which were now functions of time), and (3) subtract these new background values from the measured values. The corrections for sedimentation were made only to those particle suspensions for which an obvious decrease in absorbance versus time occurred for all four wavelengths. The absorbance curves for all four wavelengths were always parallel for a particular sedimenting sample. After background fluorescence intensities were corrected for the sedimenting suspensions, values of k_w for these samples were observed to be similar to other samples and the fluorescence intensity of rhodamine 110 was relatively constant throughout the experiment. Thus, the success of the corrections was confirmed by eliminating the experimental artifacts which initially revealed the behavior of the unstable particle suspensions.

Binding of Perylene by Dissolved and Adsorbed Humic Substances. A nonlinear least-squares curve-fitting program was used to fit equation (4.1) to the measured fluorescence intensities of all the samples spiked with perylene, and the extrapolated initial fluorescence values at time zero were determined (Figure 2). Partition coefficients and quantum yields for the perylene-DOM complexes (i.e., K_{oc}, ϕ) were determined by analyzing the initial fluorescence intensities of humic material blank solutions using equation (4.5). Results for a typical experiment are shown in Figure 3a, in which the normalized fluorescence intensities obtained

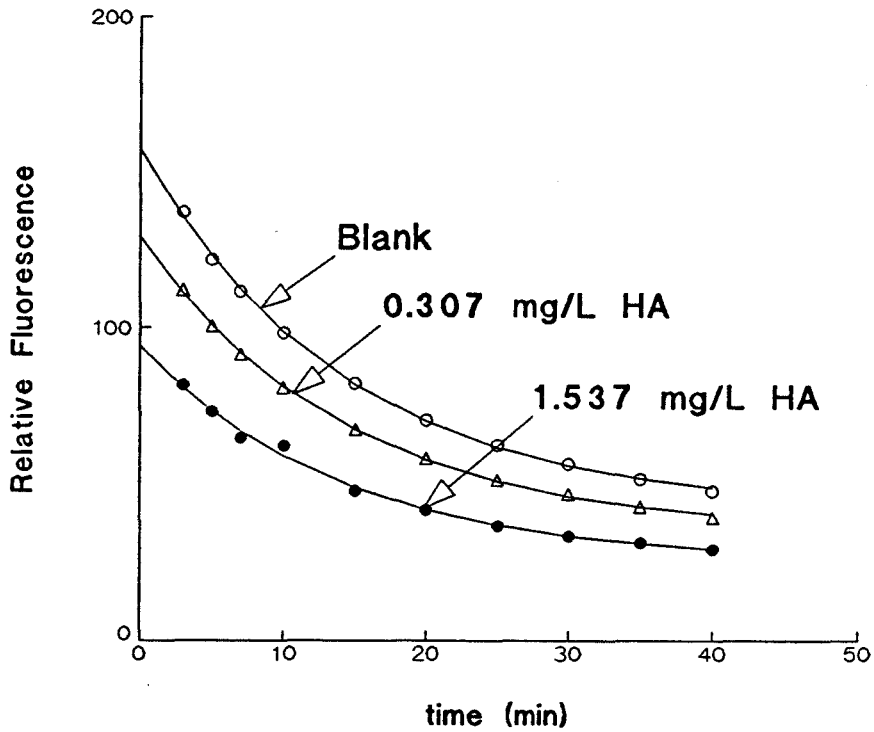


Figure 2. Perylene binding by dissolved humic acid in 0.1 M NaCl solutions at pH 4. Nominal perylene concentration for each sample is 0.4 μg/L (1.6 nM). Each curve shows the adsorption of perylene to cell walls versus time.

from back-extrapolation to t = 0 are plotted as a function of DOM concentration.

The samples containing both dissolved and adsorbed humic material were analyzed similarly with equation (4.1) to determine fluorescence values at time zero. The values of K_{oc} and ϕ obtained from the humic material blank solutions and the respective fractions of free and adsorbed humic substances (i.e., [OC] and $[OC]_B$) obtained from TOC analysis were then utilized in equation (4.10) in order to determine partition coefficients and quantum yields for the humic substances which were adsorbed to aluminum oxide particles (i.e., K_{oc}^B, ϕ_B). Figure 3b shows the results for a typical study; the homogeneous data (no alumina present) are replotted from Figure 3a for comparison. For the same total amount of humic acid, the presence of aluminum oxide particles diminished the ability of humic acid to bind perylene. For this particular system, the association of the probe with dissolved humic acid was nearly two times that with the humic acid adsorbed on alumina surfaces.

The method above was used to determine all partition coefficients for the humic substances which were adsorbed to aluminum oxide surfaces. The method assumes that the humic substances which are not adsorbed to alumina have the same properties and characteristics as the humic material blank solutions, and thus the partition coefficients and quantum yields of the dissolved material can be utilized to calculate the partition coefficients and quantum yields of the adsorbed material. The major criterion for this method, therefore, is that the adsorption process does not fractionate the humic substances.

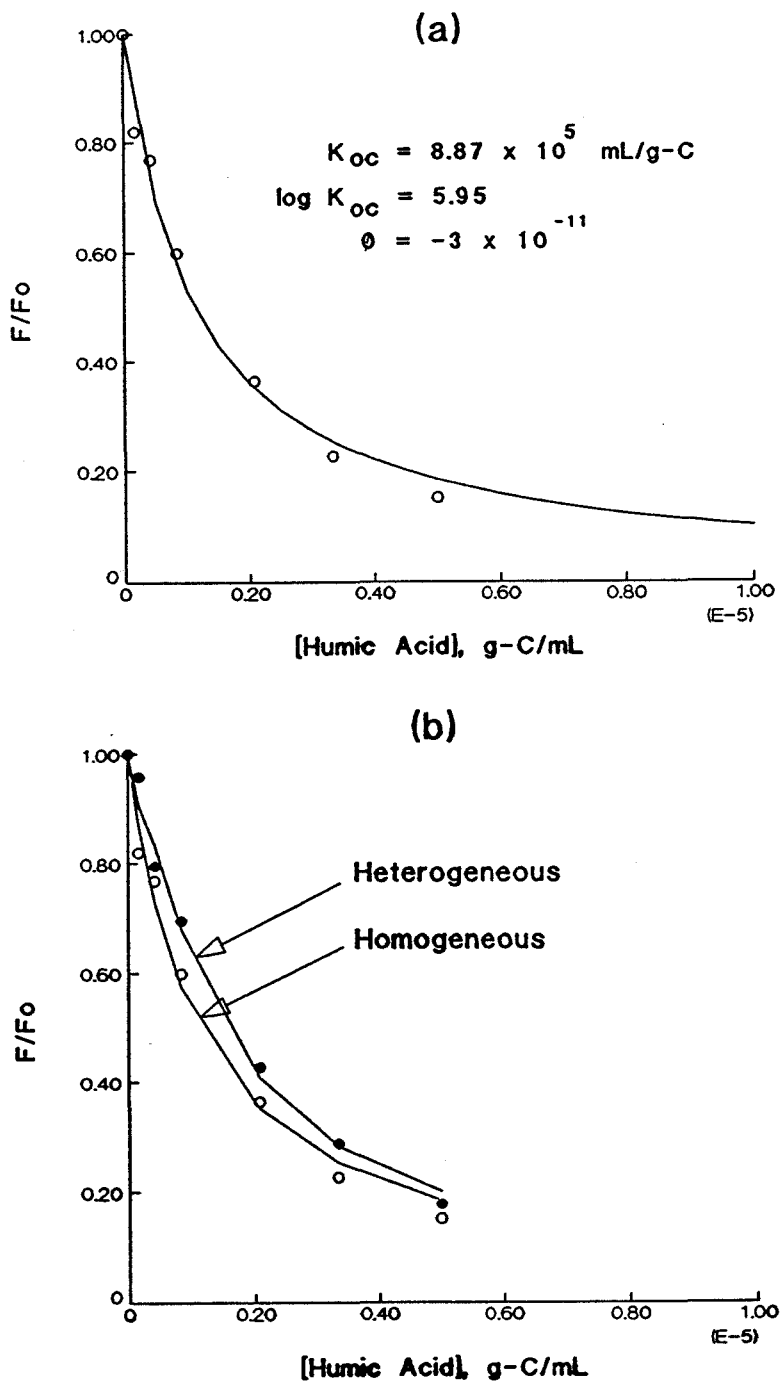


Figure 3. **Perylene binding by humic acid in 0.1 M NaCl samples at pH 4. Nominal perylene concentration for each sample is 0.4 μg/L (1.6 nM). a) Perylene fluorescence as a function of total humic acid for homogeneous samples (i.e., all humic acid is dissolved in solution). b) Comparison of homogeneous samples with heterogeneous samples (i.e., those containing both dissolved and adsorbed humic acid).**

Humic substances are by definition a complex, heterogeneous mixture of organic compounds; they comprise one of the most widely distributed classes of natural products on Earth (Aiken et al., 1989). Humic substances are heterogeneous with respect to the diversity of molecules that compose the mixture, and with respect to the diverse functional groups, structural units, and configurations that compose individual molecules (Leenheer et al., 1989). Because of the heterogeneous nature of humic materials, the use of "average" chemical and physical properties to characterize their reactions in the environment may not be valid. For example, Davis and Gloor (1981) found that higher molecular weight DOM was preferentially adsorbed to an aluminum oxide surface; thus, the process of adsorption fractionated the DOM with the more hydrophobic compounds adsorbed to the alumina surface and the more hydrophilic compounds remaining in solution.

Although the humic substances used in this research were isolated fractions (Malcolm et al., 1989), they still are not homogeneous mixtures. This can be shown by comparing the different types of molecular weights determined for both humic and fulvic acid:

$$DP = \frac{M_w}{M_n} \tag{4.14}$$

where DP is the degree of polydispersity, and M_w and M_n are the weight-average and number-average molecular weights, respectively. The degree of polydispersity is often used in polymer science as an indicator of sample dispersity. For a monodisperse

sample, DP has a value of unity. From molecular weight measurements of the humic substances used in this study (Aiken et al., 1989; Beckett et al., 1987; Reid et al., 1990), the degree of polydispersity is approximately 1.66-1.83 for fulvic acid and 2.78-3.87 for humic acid.

From the polydispersity data, therefore, it can be seen that neither Suwannee River humic acid nor fulvic acid are homogeneous mixtures. The method used by Beckett et al. (1987) to determine molecular weights (field flow fractionation or FFF), in fact, utilizes the ability to fractionate mixtures based on the different diffusion coefficients of sample species. An empirical size fractionation of Suwannee River humic acid has also been accomplished with gel permeation chromatography (Green et al., 1992).

If significant fractionation of the humic substances by adsorption onto alumina occurred in this study, the method utilized to determine K_{oc}^{B} and ϕ_B would not be valid. Murphy et al. (1990) examined whether the fractionation of Suwannee River humic acid could be detected in an adsorption/partitioning experiment. In their experiment, Suwannee River humic acid was sequentially reacted with hematite to determine if the characteristics of the humic coating would change upon sequential adsorption to clean mineral surfaces; the nonsorbed supernatant in each batch reaction was used for the subsequent reaction with clean hematite. They postulated that if fractionation occurred, both the extent of humic acid adsorption onto hematite and the cosorption of a hydrophobic compound would not remain constant for the sequential reactions. However, they found that neither the fractional adsorption of

humic acid nor the relative amount of the hydrophobic compound bound by the humic-coating changed significantly between successive batch experiments.

The results of Murphy et al. (1990) show that Suwannee River humic acid does not fractionate appreciably upon adsorption to a mineral surface. They concluded that the characteristics of the humic acid which affect its adsorption to mineral surfaces and its ability to bind hydrophobic compounds are uniform. Therefore, the method utilized in this study to determine K_{oc}^{B} and ϕ_B should be valid; although Murphy et al. (1990) did not examine fulvic acid, it should not fractionate in the present study because it is less polydisperse than Suwannee River humic acid, as shown by its lower degree of polydispersity. This assumption is supported by the observations of Aiken et al. (1989). They reported that although Suwannee River fulvic acid is definitely a heterogeneous mixture, the material in water is relatively monodisperse with respect to size and weight.

The partition coefficients for perylene binding to dissolved and adsorbed humic material are listed in Table V for the conditions which were investigated. The effects of varying aqueous chemistry conditions and of adsorbing humic material onto the aluminum oxide surface on the partitioning of perylene are summarized in Figure 4. Only a few experiments (pH 4) were performed with fulvic acid because of its lower ability to bind perylene and its lower adsorption to aluminum oxide particles relative to humic acid (Chapters 2 and 3). The respective partition coefficients were determined utilizing the methods described above.

Table V. Partition Coefficients and Quantum Yields for Perylene and Humic Substances.[a]

		Dissolved Humic Substance		Adsorbed Humic Substance	
		K_{oc} ($x10^{-5}$)	ϕ ($x10^{12}$)	K_{oc}^{B} ($x10^{-5}$)	ϕ_B ($x10^{12}$)
Humic Acid					
pH 4	0.001M NaCl	11.279	(4)	6.678	1
	0.01M NaCl	10.314	1	4.469	< 1
	0.1M NaCl	8.869	(30)	4.719	1
	1 mM Ca^{2+} [c]	9.292	< 1	5.474	2
pH 7	0.001M NaCl	9.582	< 1	< 0.31[b]	90
	0.01M NaCl	8.991	(« 1)	< 0.29	100
	0.1M NaCl	4.689	« 1	< 0.15	100
	1 mM Ca^{2+} [c]	4.096	< 1	1.036	100
pH 10	0.001M NaCl	5.096	(2)	< 0.15	10^4
	0.01M NaCl	1.946	« 1	< 0.07	100
	0.1M NaCl	0.716	2	< 0.06	100
	1 mM Ca^{2+} [c]	0.601	20	0.273	10
Fulvic Acid					
pH 4	0.001M NaCl	1.494	600	< 0.03	$3x10^6$
	0.01M NaCl	1.374	70	< 0.02	$4x10^6$
	0.1M NaCl	1.194	90	< 0.02	$2x10^6$
	1 mM Ca^{2+} [c]	1.276	70	< 0.03	$2x10^6$

[a] Units of K_{oc}, K_{oc}^{B} are mL/g-C. (ϕ) denotes negative value. [b] Indicates no binding observed. Value shown is a calculated upper limit based on the standard deviation of fluorescence measurements for the dissolved humic substances. [c] 0.1 M total ionic strength.

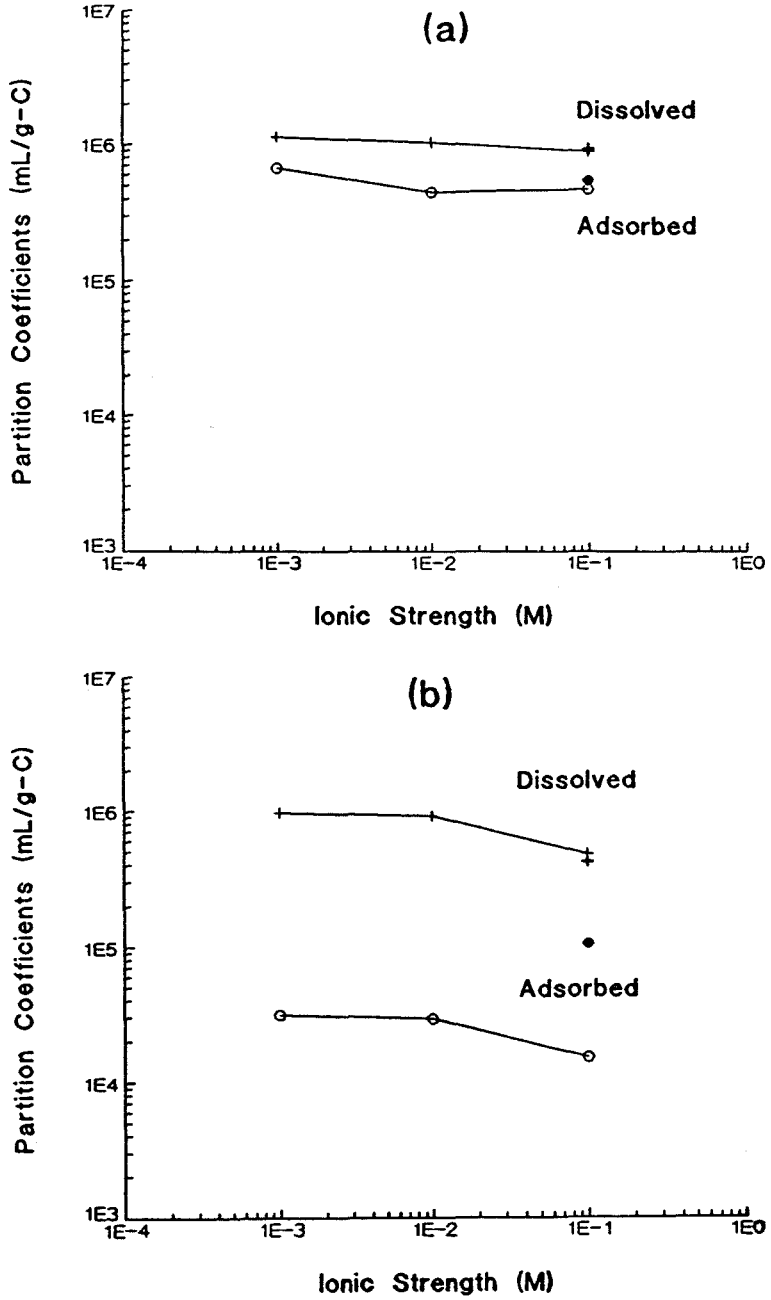


Figure 4. Binding of perylene by dissolved and adsorbed humic material. Symbols connected by lines are experiments in NaCl solutions. Single (**bold**) points at 0.1 M ionic strength refer to experiments with 1 mM Ca^{2+}. a) Partition coefficients for humic acid versus ionic strength at pH 4. b) Partition coefficients for humic acid versus ionic strength at pH 7. Coefficients for adsorbed humic acid in NaCl samples are upper estimates (See text and Table V).

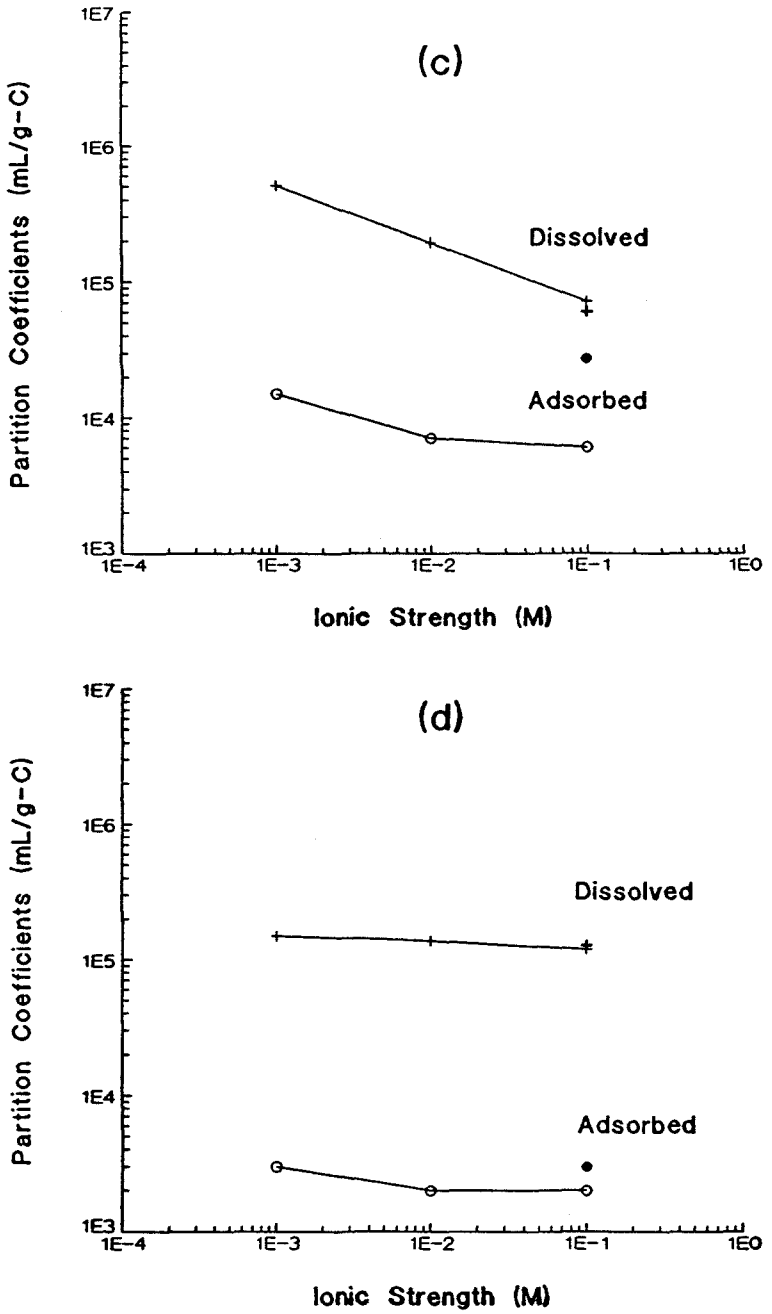


Figure 4. Binding of perylene by dissolved and adsorbed humic material. Symbols connected by lines are experiments in NaCl solutions. Single (**bold**) points at 0.1 M ionic strength refer to experiments with 1 mM Ca^{2+}. c) Partition coefficients for humic acid versus ionic strength at pH 10. Coefficients for adsorbed humic acid in NaCl samples are upper estimates (See text and Table V). d) Partition coefficients for fulvic acid versus ionic strength at pH 4. Coefficients for all adsorbed fulvic acid samples are upper estimates (See text and Table V).

Partition coefficients for perylene binding to dissolved humic acid showed a large dependence on pH and NaCl concentrations. As the pH increased from 4 to 10 for a constant ionic strength, a decrease in the binding of perylene was observed for all dissolved humic acid samples (Table V). For example, at fixed ionic strengths, K_{oc}(HA) decreased 50 to 95% when the pH was raised from 4 to 10 with the biggest decrease occurring at 0.1 M NaCl. Increases in the NaCl concentration caused a decrease in the partition coefficients for dissolved humic acid regardless of pH (Table V, Figure 4a,b,c); an increase in the ionic strength from 1 mM NaCl to 0.1 M NaCl decreased K_{oc}(HA) 20 to 85% for fixed pH values, with the greatest decrease observed at pH 10.

The ability of fulvic acid to bind perylene showed a similar dependence (20% decrease) on increasing NaCl concentration at pH 4 (Table V). However, because partition coefficients for dissolved fulvic acid were almost an order of magnitude smaller than K_{oc}(HA) for identical solution conditions, only a barely perceptible decrease in K_{oc}(FA) is observed with increasing ionic strength (Figure 4d).

The presence of Ca^{2+} had little effect on the binding of perylene by either DOM when compared to NaCl solutions of the same ionic strength (Figure 4). For example, 1 mM Ca^{2+} (0.1 M total ionic strength) at pH 7 and 10 caused a small decrease in the ability of dissolved humic acid to bind perylene (13 and 16%, respectively), while both humic and fulvic acid showed a slight increase (5 and 7%, respectively) in the partition coefficient at pH 4 (Table V).

The effects of aqueous chemistry on perylene binding by the dissolved humic substances used in this study have been discussed in Chapter 2. Briefly, variations in solution chemistry cause changes in the aqueous activity coefficient of the hydrophobic probe perylene, as well as changes in the conformation and polarity of DOM. Although the aqueous activity coefficient of perylene is the most important parameter overall for determining order-of-magnitude effects, it is not as sensitive to changes in solution chemistry as are the conformation and polarity of dissolved humic materials, which subsequently affect the hydrophobic environment of DOM and its ability to bind nonpolar organic molecules.

At constant ionic strength, for example, increases in pH progressively deprotonate DOM molecules but have little effect on the aqueous activity coefficient of nonpolar organic molecules (i.e., $\gamma_i^w \approx$ constant). Deprotonation increases the polarity of DOM and decreases its hydrophobicity and ability to bind perylene. For fixed pH values, increases in electrolyte concentrations tend to "salt out" hydrophobic organic compounds (i.e., γ_i^w increases) but also compress DOM molecules by electrostriction (Leenheer et al., 1989). This compression decreases the size of the voids in dissolved humic material into which perylene can partition. Because the DOM is affected more than perylene's activity coefficient by the increase in electrolyte, the amount of the probe bound by DOM decreases.

In order to study the ability of organically-coated mineral surfaces to bind perylene, experiments were carried out in which humic substances were adsorbed to aluminum oxide particles. To facilitate comparison between the presence and

absence of the hydrous oxide surface, experimental conditions were identical to those for the homogeneous systems.

In all cases, the presence of the aluminum oxide surface decreased the ability of humic and fulvic acid to bind perylene. At pH 4, the partition coefficients for adsorbed humic acid were 45 to 60% of those for dissolved humic acid at identical NaCl concentrations (Table V, Figure 4a). At pH 7 and 10, no partitioning of perylene into alumina-bound humic acid was observed regardless of NaCl concentration. Likewise, at pH 4 and various NaCl concentrations, perylene was not able to partition into surface-bound fulvic acid.

In contrast to the results observed for dissolved humic acid, the presence of 1 mM Ca^{2+} had a large effect on the adsorbed humic acid partition coefficient. For all pH values examined, the presence of Ca^{2+} increased K_{oc}^{B}(HA) and was especially significant at pH 7 and 10 (Table V, Figure 4a,b,c). For fulvic acid, however, the presence of Ca^{2+} had little effect on the alumina-bound partition coefficient, much like what was observed previously in the absence of the aluminum oxide surface.

The ability of adsorbed humic substances to bind HOC is dependent on several different parameters. Some of these parameters, such as aqueous chemistry conditions and the "quality" of the humic material (e.g., size, aromaticity, polarity), affect dissolved humic substances also, as discussed above. Another variable affecting the partitioning of compounds to surface-bound humic substances appears to be the mechanisms by which humic substances are adsorbed to hydrous oxide surfaces. The mechanisms of adsorption for humic substances onto mineral surfaces are discussed

by Sposito (1984, 1989), and the adsorption of Suwannee River humic material onto aluminum oxide has been discussed for these particular systems in Chapter 3.

At pH 4, adsorbed fulvic acid did not measurably bind perylene, although the fluorescent probe did partition into dissolved fulvic acid appreciably (Figure 4d). In Chapter 3, it was argued that fulvic acid adsorbs to aluminum oxide particles principally through a ligand-exchange mechanism for the conditions studied here. Enhanced adsorption of fulvic acid by a hydrophobic-bonding mechanism does not occur because fulvic acid is relatively hydrophilic and because most of the fulvic carboxyl groups are postulated to be bound directly to the surface. Since its carboxyl groups form inner-sphere complexes with Al(III), adsorbed fulvic acid molecules are bound tightly to the alumina surface. This, along with the relatively small size of fulvic acid molecules (800 daltons), severely restricts any fulvic acid conformational changes necessary to bind perylene. The conformational entropy effects may be considered as analogous to those observed with polymer adsorption on surfaces; high molecular weight polymers adsorb preferentially to smaller ones at equilibrium because of their smaller conformational entropy loss on adsorption and their greater opportunities to form favorable contacts with the surface (O'Melia, 1988).

The presence of 1 m$\underline{M}$ Ca^{2+} (0.1 $\underline{M}$ total ionic strength) at pH 4 had little effect on the ability of adsorbed fulvic acid to bind perylene. This is not surprising, based on the postulated adsorption mechanisms for fulvic acid described above and in Chapter 3. The presence of bivalent cations has little effect on the adsorption of fulvic acid because of its relatively small size and hydrophilic character and because

most of its anionic functional groups (i.e., carboxyl groups) are postulated to be bound directly to the surface as inner-sphere complexes. The lack of enhanced fulvic acid adsorption to alumina and perylene binding by adsorbed fulvic acid in the presence of Ca^{2+} both relate to the absence of significant hydrophobic effects among adsorbed fulvic acid molecules.

The pH and ionic strength dependence of the adsorbed humic acid's ability to bind perylene in NaCl solutions is a similar, albeit magnified, effect to that observed for dissolved humic acid. As described above, the additional effects relative to those for the dissolved species are postulated to result from the mechanisms by which the humic acid is adsorbed to the aluminum oxide surface.

Ligand exchange is thought to be the major adsorption mechanism for humic acid for all solution compositions. In contrast to fulvic acid, however, other mechanisms contribute to the adsorption of humic acid (Chapter 3). In NaCl solutions, for example, hydrophobic bonding appears to be operative at pH 7 and, particularly, at pH 4 while Na^+ bridging becomes important at pH 10.

In the absence of bivalent cations, there is significant binding of perylene by adsorbed humic acid only at pH 4 (Table V). Partitioning of the probe can occur because of the relatively low polarity of humic acid at this pH value, and because a fraction of the humic acid is adsorbed on aluminum oxide particles by relatively weak hydrophobic bonding forces. Also, because the hydrophobic attraction between humic acid and the alumina surface is relatively weak, the adsorbed molecules may be able to change their conformation at the surface if necessary to bind perylene. Finally,

although ligand exchange is the predominant mechanism by which humic acid is adsorbed to alumina at this pH, the larger size of humic acid relative to fulvic acid may allow the tightly-bound molecules to assume more favorable conformations at the surface. Although the ability to change its conformation must help adsorbed humic acid in binding perylene, it is not as effective as if the humic acid molecules were freely dissolved (Figure 4).

In NaCl solutions, partitioning of perylene into adsorbed humic acid is not observed at pH 7 and 10. At these pH values, the polarity of humic acid molecules is much higher than at pH 4. The adsorbed humic acid most likely is bound tightly at the alumina surface by inner-sphere complexes because hydrophobic bonding is not postulated to be a major adsorption mechanism at these pH values. Although Na^+ bridging may occur at pH 10 (forming outer-sphere complexes), the higher polarity of humic acid will tend to restrict conformational changes even for these weakly-bound molecules. Therefore, although freely dissolved humic acid is capable of binding perylene at neutral to high pH values, the combination of high polarity and restricted conformations at the aluminum oxide surface prove to be too unfavorable for binding of the probe by the adsorbed species.

As shown in Figure 4, the presence of 1 mM Ca^{2+} at a total ionic strength of 0.1 M has a large effect on the adsorbed humic acid partition coefficient. Adding Ca^{2+} ions to the solution has two major effects on the operative adsorption mechanisms for humic acid: (*i*) at pH 10 (and possibly at pH 7) it enables water bridging to occur and (*ii*) it helps decrease electrostatic repulsion in the adsorbed

layer at all pH values (Chapter 3). The decrease in electrostatic repulsion, in turn, enables more hydrophobic bonding to occur at pH 4 and 7. As the pH increases in these systems, adsorbed humic acid is expected to be less tightly-bound to alumina surfaces and its characteristics, therefore, should become more like those of the dissolved species. In Figure 4, this is exactly what is observed. As the pH increases in the presence of Ca^{2+}, K_{oc}^{B} is seen to approach the values of K_{oc} for humic acid. This is not too surprising because, logically, weakly-adsorbed humic material should have properties approaching those of their dissolved counterparts, while strongly adsorbed NOM will be less like dissolved material.

The decrease in the binding of perylene observed in this study by adsorbed humic substances relative to the dissolved species is similar to the results obtained by Garbini and Lion (1985). They examined the partitioning of the relatively volatile compounds trichloroethylene and toluene to a commercial humic acid and to alumina particles coated with the same material and observed that binding of the solutes by dissolved humic acid was nearly three times that by alumina-bound humic acid. They hypothesized that the observed reduction was because of differences in the physical and/or chemical characteristics of free versus adsorbed humic acid, selective adsorption of certain fractions of humic acid (i.e., fractionation), and/or uncontrolled solution chemistry conditions.

Several problems with the study of Garbini and Lion (1985), however, limit its usefulness in relation to natural aquatic systems. The organic substances utilized in their study were commercial humic acids which were not purified prior to use. The

use of commercial humic acids as analogues of NOM has been criticized because the commercial materials have extremely high ash contents and are not generally representative of NOM (Malcolm and MacCarthy, 1986; Chiou et al., 1987; MacCarthy and Malcolm, 1989). The method used to bind the humic acid to alumina surfaces involved drying the coated particles at 105°C. The effect of this procedure on the results is uncertain, but does not represent naturally-occurring processes. Finally, it is unclear if the behavior of significantly hydrophobic pollutants can be predicted from the volatile, and appreciably soluble, organic compounds used by Garbini and Lion (1985); this last concern, however, is probably unwarranted considering the similar results obtained in this study for perylene.

In contrast to Garbini and Lion (1985), solution chemistry was controlled in this study. Also, fractionation was not expected to occur for the materials utilized here based on the observations of Murphy et al. (1990). Therefore, although the magnitudes of these two effects are unclear in the work of Garbini and Lion (1985), they were insignificant in this study. The reduction in the ability of adsorbed humic substances to bind perylene relative to the dissolved material appears to result from the different characteristics of adsorbed versus dissolved NOM. The mechanisms by which humic substances are adsorbed to mineral surfaces control the magnitude of these changes. For example, the properties of weakly-adsorbed NOM tend to approach those of dissolved material as observed in Figure 4. In all cases, however, the binding capacity of NOM is expected to be reduced by the presence of mineral surfaces because of the conformational entropy losses upon adsorption. Finally, even

for weakly-adsorbed NOM, the regions of the molecules involved in binding with the surface (i.e., through hydrophobic bonding) are most likely the same regions which are important for binding of hydrophobic organic compounds. Upon adsorption to mineral surfaces, therefore, these sites are then unavailable for binding nonpolar compounds.

It is unclear how important the effects of adsorbed NOM may be in determining the partitioning of HOC in natural water systems. Backhus and Gschwend (1990) examined groundwater samples from a site recharged with secondary-treated sewage in order to determine the in situ organic material's ability to bind perylene. They observed that samples from wells within the contaminant plume showed temporal variation in the ability of the organic material present to bind perylene. They postulated that the temporal variability in K_{oc} values may have resulted from compositional or configurational differences in the organic material or from varying solution composition. They concluded that the organic material which did not bind perylene, although present at roughly the same concentrations and composed of similar structural elements, was simply "denatured" and unable to bind the probe.

A possible explanation for the observations of Backhus and Gschwend (1990) can be proposed based on the results of this study, as well as the results of Garbini and Lion (1985). It is conceivable that the temporal variation in the organic material's ability to bind perylene depended on whether the organic substances present were freely dissolved species or whether they were adsorbed to mineral

surfaces. For the pH values of the groundwater samples (pH~6), the difference in observed partition coefficients could be significant as shown in Figure 4b and Table V, particularly if bivalent cations were not present. Although the groundwater samples examined by Backhus and Gschwend (1990) were believed to contain organic colloids and/or inorganic colloids with organic coatings, analysis and characterization of the organic material in solution versus that on particle surfaces were not made. Also, solution concentrations of major ions in the samples were not reported. Therefore, the hypothesis that adsorption of the organic substances to mineral surfaces was the process that "denatured" the material cannot be substantiated.

A final point worth noting concerns the methods which have been utilized to investigate the binding of HOC by adsorbed NOM. The techniques used by Garbini and Lion (1985) (equilibrium headspace analysis) and Murphy et al. (1990) (centrifugation followed by ^{14}C counting) both are subject to errors resulting from solute adsorption to the bare mineral surface.

Curtis et al. (1986) performed sensitivity analysis on the relative contributions of solute adsorption on mineral surfaces and solute binding by organic matter for HOC without functional groups. They showed that adsorption to mineral surfaces becomes more important for increasingly soluble organic compounds, decreasing values of f_{oc}, and increasing specific surface area of the bare mineral. Thus, the dominance of one or the other contribution to hydrophobic solute binding depends on K_{ow}, K_{oc} and/or K_{oc}^{B}, f_{oc}, and the surface area of the mineral sorbent which is exposed to the solute.

Murphy et al. (1990) recognized the potential importance of adsorption to mineral surfaces in their system and attempted to remove this contribution to solute binding by performing mineral blank (i.e., sorbent with no organic coating) experiments. As they noted, a rigorous calculation of the mineral surface contribution to solute binding requires that the exposed (i.e., bare) surface area of the (partially) organically-coated mineral be known. Based on the assumption that plateaus in adsorption density isotherms corresponded to monolayer coverages, they calculated fractional coverages of the organic coatings on mineral surfaces for each data point.

A correction of this type, however, has the potential for many errors and is extremely dependent on the assumptions made. For example, Murphy et al. (1990) assumed that the organic coatings were uniform on hematite particles, but that humic material adsorption was limited to the edge sites of kaolinite. This meant that most of the kaolinite surface comprising the basal plane was assumed not to be covered with an organic coating. Therefore, while fractional coverage of hematite was estimated to vary from 1 to 96% with increasing f_{oc}, the organic coverage of kaolinite ranged from 7% to approximately two monolayers only on the edge sites. As might be expected, the corrections made by Murphy et al. (1990) for solute adsorption to kaolinite were larger than to hematite because more of the mineral surface was exposed. Also, the correction for mineral adsorption had the greatest effect at the lowest values of f_{oc} (i.e., lowest coverages of organic coating). It is uncertain how significant the errors may be in using the correction procedure of Murphy et al. (1990); they found, for example, that the K_{oc} values

calculated were relatively insensitive to the estimated exposed surface area of the minerals.

In their study of toluene and trichloroethylene binding by organically-coated alumina particles, Garbini and Lion (1985) did not account for the possibility of solute adsorption to bare alumina surfaces. Although Garbini and Lion (1985) used relatively high organic carbon mass fractions (f_{oc} values of 0.40 and 0.54) in their experiments, the calculations of Curtis et al. (1986) indicate that solute adsorption to the alumina surface may have been important. Adsorption to the alumina surface may have been significant because of the appreciably soluble (and volatile) organic solutes used by Garbini and Lion (1985).

In contrast to the methods used by Murphy et al. (1990) and Garbini and Lion (1985), the technique (fluorescence quenching) utilized in this study to investigate the binding of perylene by alumina-bound humic material is not subject to errors resulting from adsorption of the probe to inorganic surfaces. The fluorescence quenching method determines only the amount of the fluorescent organic probe associated with NOM. This is because an inorganic surface, such as aluminum oxide, cannot quench the fluorescence of organic molecules which are merely adsorbed onto it (Chapter 2). The use of inorganic materials as substrates for studying the photochemistry of adsorbed organic molecules and the use of fluorescent organic molecules to probe the solid-liquid interfacial region of inorganic colloids has been extensively documented (Kalyanasundaram, 1987).

Kinetics of the Partitioning Reaction. Using the fluorescence quenching method of Backhus and Gschwend (1990), the kinetics of the binding reaction are observed indirectly because of the competing reactions (association with NOM versus adsorption to the fluorescence cell walls). In a sense, the rate of PAH binding by NOM must be known a priori because a key assumption of the technique is that the rate of PAH binding by NOM is fast relative to the rate of PAH adsorption to the cell walls. By allowing the partitioning reaction to reach equilibrium before the initial measurement is taken, subsequent decreases in fluorescence are then attributed to adsorption of the PAH to cell walls.

In the presence and absence of NOM, measurements of the perylene fluorescence intensity decreased exponentially with time, in accordance with equation (4.1). The binding of perylene by dissolved and adsorbed humic material was observed to be relatively fast; the distinct and parallel curves obtained for various concentrations of NOM (e.g., Figure 2) indicated that the binding of perylene by the NOM was complete within 3 minutes, the time allotted before taking the first measurement.

The relatively fast rates observed for perylene binding by dissolved and adsorbed humic substances agree with previous studies of the kinetics of PAH partitioning to DOM. No kinetic information has been reported, however, for the binding of hydrophobic organic compounds by well-characterized, organically-coated hydrous oxide surfaces.

In Chapter 2, it was reported that the binding of anthracene and pyrene by the

dissolved humic material utilized in this study was observed to be very fast. Association appeared to be complete within 20 seconds for many samples, and never took longer than 3 minutes to reach an apparent equilibrium. Gauthier et al. (1986) found that equilibration of PAH solutions (anthracene, phenanthrene, pyrene) after adding DOM was very rapid, requiring less than 1 minute. McCarthy and Jiminez (1985) observed that the rate of binding of benzo[a]pyrene by Aldrich humic acid was also rapid. An apparent equilibrium was obtained within 5 to 10 minutes after the addition of DOM. Backhus and Gschwend (1990) found that the association of perylene with Aldrich humic acid, bovine serum albumin, and unaltered groundwater samples containing NOM was complete within 3 minutes. As discussed above, the groundwater samples were believed to contain organic colloids and/or inorganic colloids with organic coatings.

The kinetic results observed above for the binding of perylene by adsorbed humic material contrast with those using sediments and soils as sorbents. The times required to attain sorption equilibria in the latter systems are usually reported to be from hours to days, but in reality may proceed indefinitely (Karickhoff, 1984). Karickhoff (1980) has proposed that there are two kinetically distinct components to sorption reactions onto sediments, a rapid component requiring at most a few minutes to reach equilibrium and a much slower component requiring up to weeks to equilibrate. The latter component is thought to reflect an intraparticle process whereby a compound is slowly incorporated into either particle aggregates or sorbent components (Karickhoff, 1984). The incorporation into the sorbent matrix is

contemplated as being responsible for the relative resistance to extraction observed for some sorbed chemicals. This behavior is exemplified by the increasingly difficult recovery of sorbed compounds as the incubation time increases; observations of the phenomena have been described as an "aging" of the sorbed compound (Voice and Weber, 1983).

The differences observed between binding of hydrophobic organic compounds by DOM and by soils and sediments have been attributed previously to the presence of mineral surfaces and/or high molecular weight organic material in soils and sediments (Karickhoff, 1984). For example, organic material existing in sediments and soils consists of relatively insoluble, high molecular weight macromolecules compared to organic material which is present in natural waters (i.e., the humic substances used in this study). While molecular weights of aquatic humic acids are generally in the range from 1000 to 10,000, those for soil humic acids have been reported to be from 2600 to more than 1 million (Kile and Chiou, 1989), and the largest fraction of humic substances in lake sediments falls into the molecular weight ranges 5000-100,000 and >100,000 (Ishiwatari, 1985).

Organic substances in sediments and soils, therefore, may be composed of material similar to the humin-kerogen structures proposed by Freeman and Cheung (1981). They hypothesized NOM in sediments to be a humic-kerogen gel affixed to mineral surfaces and pictured it as highly branched polymer chains forming complex three-dimensional networks. Absorbed liquids in these systems would cause the network to swell and form a gel. Diffusion of organic solutes into such a

three-dimensional network and their subsequent incorporation into a gel would agree with the slower observed rates for partitioning into sediment and soil organic matter.

The slow rates of binding of hydrophobic organic compounds by sediments and soils have also been attributed to adsorption of the compounds by mineral surfaces. For example, Ball and Roberts (1991a,b) found that sorption of organic chemicals onto sandy aquifer material required contact times on the order of tens to hundreds of days to reach equilibrium, with physical adsorption to mineral surfaces the most significant contribution to the total amount sorbed. The rate of sorptive uptake was modeled successfully with an intraparticle diffusion model incorporating retarded transport in the constricted internal pores. This interpretation concurred with the observation that extremely long extraction times (230 days) were required to recover the sorbed compounds from unaltered material, while a shorter time (30 days) was sufficient for extracting pulverized material.

As discussed earlier, however, the fluorescence quenching technique utilized in this study to investigate the binding of perylene by alumina-bound humic substances does not measure adsorption of the fluorescent probe to the aluminum oxide surface. Therefore, the rates observed here are indicative only of the partitioning reaction to NOM. It is realistic to believe that any adsorption of perylene that was occurring on the bare surfaces of the aluminum oxide particles was much slower, based on the loss of the organic probe to the fluorescence cell walls. For example, it appeared that an apparent equilibrium for perylene adsorption to the cell walls was reached only after a contact time of a few hours (Chapter 5).

Quenching Efficiency. The quantum yields obtained for perylene associated with dissolved humic and fulvic acid (Table V) are thought to be accurate since relatively large decreases in the fluorescence ratio are observed with increasing concentrations of DOM. All curves obtained using Equation (4.5) for the various perylene-DOM systems asymptotically approached quantum yields of zero as [OC] $\Rightarrow \infty$. Most quantum yields for the adsorbed humic substances, however, are not credible because of the absence of significant binding of perylene. The only reliable values of ϕ_B are those at pH 4 and those for systems in which Ca^{2+} was present.

Few published results are available for the quantum yields of PAH-NOM complexes. Backhus and Gschwend (1990) found that Aldrich humic acid fully quenched the fluorescence of perylene associated with it ($\phi \approx 0$), while bovine serum albumin quenched only 42 percent of the associated perylene fluorescence ($\phi = 0.58$). The observations of Gauthier et al. (1986) suggest that values of zero for ϕ are found for a wide variety of humic and fulvic acids. They argued that the appearance of linear Stern-Volmer plots indicates that binding of PAH compounds by organic matter results in complete quenching of probe fluorescence. However, as noted by Backhus and Gschwend (1990), caution must be used in interpreting Stern-Volmer plots. For example, any deviations from linearity may be subtle and easily overlooked, particularly if there is significant scatter in the data or if the ratio F_0/F is relatively low (< 1.2) as shown in Chapter 2.

SUMMARY AND CONCLUSIONS

This study investigated the ability of Suwannee River humic substances which were adsorbed on an aluminum oxide surface to bind a fluorescent organic probe relative to the freely dissolved humic material. It was postulated that the mechanisms by which the humic substances are adsorbed to mineral surfaces greatly influence the ability of the adsorbed humic material to bind nonpolar hydrophobic pollutants. Because the adsorption mechanisms are affected by solution chemistry, a systematic study of the influence of pH, ionic strength and background electrolyte composition on carbon-normalized partition coefficients was performed.

A fluorescence quenching technique was utilized to quantify the amount of the nonpolar hydrophobic probe which was bound by adsorbed and dissolved humic material. The binding of perylene by dissolved and adsorbed humic substances was observed to be relatively fast; an apparent equilibrium was obtained within 3 minutes after spiking the samples with the probe. The fluorescence quantum yields for perylene associated with the dissolved humic substances approached zero for the systems examined. Although the quantum yields for the adsorbed humic material-perylene complexes also approached zero, they may not be credible because of the low amount of perylene which was bound.

In the absence of an aluminum oxide surface, both humic and fulvic acid were able to bind the organic probe perylene. The binding of perylene by dissolved humic acid showed a large dependence on pH and NaCl concentrations. Partition coefficients for dissolved humic acid decreased with both increasing pH (fixed ionic

strength) and increasing ionic strength (fixed pH). The ability of dissolved fulvic acid to bind perylene showed a similar dependence on increasing ionic strength; however, the partition coefficient for fulvic acid was almost an order of magnitude smaller than that for humic acid for identical solution conditions. The presence of Ca^{2+} had little effect on the binding of perylene by either of the dissolved humic substances.

For all systems examined, adsorption of the humic substances on aluminum oxide decreased the ability of humic material to bind perylene. At pH 4, the partition coefficients for adsorbed humic acid were approximately half the values of those for dissolved humic acid. At higher pH values, partitioning of perylene into alumina-bound humic acid was not detected. Likewise, at pH 4 perylene was not able to associate with alumina-bound fulvic acid. In contrast to the results observed for dissolved humic acid, the presence of Ca^{2+} greatly enhanced the binding of perylene by adsorbed humic acid.

The adsorption of humic and fulvic acid onto an aluminum oxide surface decreased their ability to bind hydrophobic organic compounds. The effect of solution chemistry, apart from its influence on changing the characteristics of the dissolved material, is to alter the mechanisms by which the humic substances adsorb to hydrous oxide surfaces. The different adsorption mechanisms, in turn, affect how tightly bound the organic material is held at the surface. The ability of weakly-adsorbed humic acid to bind perylene, and possibly many of its other properties, approaches that of the dissolved species.

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Chapter 5

SORPTION KINETICS OF A FLUORESCENT HYDROPHOBIC ORGANIC PROBE ON AN INORGANIC SILICA SURFACE

ABSTRACT

The influence of solution chemistry on the rate and extent of perylene adsorption/desorption on a fused silica surface was investigated. Fluorescence was utilized to monitor the loss of perylene from aqueous solution. The time required to reach equilibrium in adsorption reactions ranged from 2½ to 4 hours, and an apparent equilibrium was attained in 60 to 90 minutes for desorption reactions. Quantitative recovery of the adsorbed perylene from the silica surface was observed after a 5- to 10-minute methanol extraction. At constant ionic strength, the initial rate of adsorption decreased with increasing pH for all background electrolyte compositions. The observed adsorption rates were correlated with the aqueous activity coefficient of perylene and the surface speciation of silica. At low pH values, the rate of perylene adsorption appeared to depend solely on the solute activity coefficient. At neutral to high pH values, binding of cations at the silica surface became increasingly important in determining adsorption rates. Binding of Na^+ at the silica surface decreased the rate of perylene adsorption, while binding of Ca^{2+} at the surface increased the adsorption rate. From long-term adsorption data, it appears that two (or possibly more) different processes are operative in the adsorption of perylene to the silica surface. The nature of these processes is not clear, but may relate to the structure of water at the solid-liquid interface.

INTRODUCTION

Many organic chemical compounds in aqueous environments are associated with colloidal or suspended particulate matter. As a consequence, the geochemistry and, ultimately, the fate of these organic compounds are strongly dependent on chemical reactions which occur at the solid-liquid interface of particles. Examples of chemical reactions occurring at particle surfaces include the hydrolysis of organic compounds and the heterogeneous oxidation (photochemical or thermal) of organic materials. Because organic material-surface chemical reactions require association of the organic compounds of interest with a mineral surface, sorption reactions are important precursor steps. Understanding sorption processes is an especially important key to describing the fate of hydrophobic organic compounds (HOC) in natural water systems, because the fate of these compounds having water solubilities less than a few parts per million is highly dependent on their sorptive behavior. For HOC, sorption reactions can greatly affect the mobility, bioavailability, reactivity and toxicity of the compounds.

The partitioning of nonionic hydrophobic organic compounds in surface soils and sediments has been shown to depend primarily on the hydrophobicity of the compound and the fraction of organic carbon (f_{oc}) in the sorbent (Means et al., 1980; Karickhoff et al., 1979; Chiou et al., 1979, 1981). For sorbents with adequate amounts of organic carbon, normalizing observed partition coefficients by f_{oc} results in organic carbon partition coefficients (K_{oc}) which generally vary only by factors of three to five for a given solute. However, when little organic carbon is present in a sediment or

aquifer (f_{oc} < 0.001), values for K_{oc} have been observed to be higher than what would be predicted based on partitioning into organic material (Schwarzenbach and Westall, 1981; Curtis et al., 1986b; Ball and Roberts, 1991a,b). In these systems, mineral surfaces are thought to contribute significantly to, and may even control, the sorption of HOC.

For sorbents with low amounts of organic carbon, enhanced sorption of nonionic HOC is favored when the sorbent is a "swelling" or expandable clay material, the solutes contain polar functional groups, or (particularly) a combination of the two conditions (Karickhoff, 1984; Curtis et al., 1986a). Karickhoff (1984) showed that for HOC with polar moieties (simazine and biquinoline), more sorption than can be explained by simple organic matter partitioning theory occurs when the expanding clay matter to organic carbon ratio is higher than approximately 30:1. Pyrene, which is more hydrophobic but contains no polar functional groups, was not strongly influenced by the expanding clay. The enhanced sorption of polar HOC appears to result because the polar functional groups can participate in nonhydrophobic bonding reactions, such as hydrogen bonding, complexation, and even covalent bonding, with inorganic surfaces (Curtis et al., 1986a).

Organic compounds with polar functional groups are not the only organic solutes which can adsorb to mineral surfaces. Likewise, the sorbents need not be expandable clay minerals for adsorption in excess of organic material partitioning to occur. Schwarzenbach and Westall (1981) found that aluminum oxide, kaolinite (a non-expanding clay), and porous silica all bound halogenated and aromatic solutes

in the absence of organic carbon. An aquifer material with low f_{oc} also exhibited more sorption capacity than could be attributed to partitioning into organic material. With the exception of silica, Schwarzenbach and Westall (1981) found a highly significant positive linear correlation between the log of the binding coefficient (K_p) and log of the octanol-water partitioning coefficient (K_{ow}) for the sorbents in their study. The micropores in the surface of the porous silica were suspected to be the major cause for the poor correlation for that material. For low organic-carbon sorbents, relatively small values of K_p were obtained and the inorganic surface contribution to adsorption was found to be more weakly dependent on K_{ow} than was organic material partitioning. In the absence of organic carbon, Schwarzenbach and Westall (1981) observed that the specific surface area and the nature of the mineral surface had large impacts on the degree of sorption. Because all of the low-organic carbon samples had f_{oc} values less than 0.001, they suggested that the numerous correlations between K_{oc} and K_{ow} be used only for sorbents with $f_{oc} > 0.001$.

Curtis et al. (1986b) found enhanced sorption for five halogenated organic solutes onto sandy aquifer material with both a low surface area (0.8 m^2/g) and a low f_{oc} (0.0002). Although equilibrium was not reached in their experiments, partition coefficients were reported for 3-day sorption studies. The higher than predicted K_{oc} values for the sorbent suggested that sorption onto the mineral surfaces was a significant factor. Ball and Roberts (1991a,b) later examined the sorption of tetrachloroethene (PCE) and tetrachlorobenzene (TeCB) onto the same aquifer material utilizing a batch methodology designed to accurately measure sorption over

long equilibration periods. They found that contact times on the order of tens to hundreds of days were required to reach equilibrium, and that physical adsorption to mineral surfaces appeared to be the most significant contribution to the total amount of compound sorbed. The long equilibration period was thought to reflect a slow intraparticle diffusion process into constricted internal pores. This hypothesis was supported by the considerable internal surface area in the unaltered material, as well as the significant internal porosity which was measured. Both Curtis et al. (1986b) and Ball and Roberts (1991a,b) observed that although K_{oc} values for the low-f_{oc} sorbent were higher than predicted by organic material partitioning, the K_{oc} values did correlate positively with K_{ow}.

Keoleian and Curl (1989) examined the adsorption of tetrachlorobiphenyl by two natural kaolinite (non-expanding) clays. One clay was well crystallized, while the other was poorly crystallized. They observed that adsorption equilibrium was achieved in two hours or less, and that the adsorption data could be fitted using a one-parameter linear isotherm model. Upon normalizing the adsorption constants for the two kaolinite sorbents with the specific surface area of each clay, they found that the magnitudes of adsorption were equivalent. Keoleian and Curl (1989) remarked that, because the specific surface area measured by BET $N_{2\,(g)}$ gives the total external surface area of particles, it can be used to normalize adsorption constants for nonporous, non-expanding minerals. For expanding clays and microporous minerals, however, normalization by BET $N_{2\,(g)}$ surface area was postulated as not being useful. Keoleian and Curl (1989) concluded that the low adsorption constants for

tetrachlorobiphenyl by kaolinite and the linearity of the isotherms indicated a nonspecific physical adsorption mechanism. A calculation of Keoleian and Curl's (1989) data, for example, indicates that the maximum surface coverage observed was less than 0.1%. They postulated that hydration of the aluminum oxide surface and hydrogen bonding of water to the silanol groups of kaolinite were energetically more favorable interactions than the van der Waals energy of attraction between tetrachlorobiphenyl and the same surface functional groups.

Murphy et al. (1990) investigated the adsorption of three HOC to the bare (i.e., not organically-coated) mineral surfaces of hematite and kaolinite. Because the mineral surfaces had been pretreated to remove any small amounts of organic carbon present, the sorption of the HOC was observed to be very low. Single-concentration adsorption constants were calculated and normalized by BET $N_{2\,(g)}$ surface areas. The surface area-normalized adsorption constants were found to be higher for kaolinite than for hematite. The higher sorptivity was hypothesized to result because of the presence of the siloxane and gibbsite basal planes, which contain few ionizable hydroxyl sites and exhibit more hydrophobic characteristics, on kaolinite surfaces. In contrast to Schwarzenbach and Westall (1981) and Curtis et al. (1986b), Murphy et al. (1990) observed that adsorption constants for the different HOC on a particular mineral did not increase uniformly with K_{ow}. However, this resulted because other surface reactions in addition to hydrophobic bonding were most likely operative; only one of the HOC used by Murphy et al. (1990) was a nonpolar compound.

Curtis et al. (1986a) performed sensitivity analysis on the relative contributions of solute adsorption on mineral surfaces and solute binding by organic matter for HOC without polar functional groups. They showed that adsorption to mineral surfaces becomes more important for increasingly soluble organic compounds, decreasing values of f_{oc}, and increasing specific surface area of the bare mineral. Thus, the dominance of one or the other contribution to hydrophobic solute binding depends on K_{ow}, K_{oc}, f_{oc}, and the surface area of the mineral sorbent which is exposed to the solute.

The most extensive investigation of HOC adsorption by bare mineral surfaces to date has been by Backhus (1990). She examined the sorption of a series of HOC (polycyclic aromatic hydrocarbons (PAH) and chlorinated benzenes) to three inorganic surfaces (kaolin, silica, and alumina). Her studies indicated that adsorption was complete within approximately 10 hours and that the adsorption isotherms were linear up to aqueous phase saturation. In agreement with Schwarzenbach and Westall (1981) and Curtis et al. (1986b), Backhus (1990) observed that the association of an organic solute with an inorganic surface increased with increasing HOC aqueous activity coefficient. The adsorption of a particular HOC to a series of different inorganic surfaces resulted in similar association constants for surfaces if normalized by available surface area. Backhus concluded that the adsorption mechanism by which HOC associates with inorganic surfaces is driven primarily by changes in the interactions and organization of the solvent water and not by a specific interaction of HOC with inorganic surfaces. A similar explanation has been

used previously to describe the mechanism of HOC partitioning into organic matter (Voice and Weber, 1983).

The mechanism of partitioning results from the "hydrophobic interaction," a combination of relatively small van der Waals bonding forces and a substantial thermodynamic gradient which drives the organic molecules out of aqueous solution (Voice and Weber, 1983). The van der Waals attraction forces between organic molecules are generally dominated by London dispersion forces (induced dipole-induced dipole) with smaller or no contributions from Keesom orientation forces (dipole-dipole) and Debye induction forces (dipole-induced dipole). The thermodynamic driving force is the increase in entropy upon breakdown of the highly-structured coordination shell of water molecules surrounding the hydrophobic solute. The free energy for transfer of a hydrophobic organic solute from aqueous solution is thus proportional to the hydrophobic surface area (i.e., size) of the molecule or, alternately, the number of water molecules which must be in contact with the dissolved molecule in aqueous solution (Tanford, 1980). The hydrophobic interaction has been discussed in detail by Tanford (1980) and Israelachvili (1985).

The observation that adsorption constants for different HOC with a particular mineral surface increase uniformly with K_{ow} (Backhus, 1990; Schwarzenbach and Westall, 1981; Curtis et al., 1986b) can thus be explained by the hydrophobic interaction. For example, it has been shown in solubility and adsorption studies that the removal of each methylene group from aqueous solution contributes ~RT to the

total energy of reaction for aliphatic organic compounds (Tanford, 1980; Israelachvili, 1985; Liang and Morgan, 1990a,b).

Because of the potential importance of mineral sorption of HOC, particularly in low-organic carbon environments, the adsorption of a nonionic, nonpolar HOC by an inorganic surface was investigated in this study. A principal hypothesis was that the rate and extent of adsorption of HOC by the bare mineral surface would be dependent on the aqueous activity coefficient (γ_i^w) of the hydrophobic solute and the relative hydrophobicity of the bare mineral surface. Because both γ_i^w and the surface hydrophobicity are affected by the aqueous chemistry of natural waters, a systematic study of the effects of pH, ionic strength and the presence of bivalent cations was undertaken. For example, it has been suggested that the adsorption of organic solutes to low-carbon sorbents may depend on pH, electrolyte concentration, and adsorption of unrelated inorganic ions (Rea and Parks, 1990). The initial rate of adsorption was also postulated to be dependent on the mixing of the sample solutions; however, because stirring rates were not quantified, the different rates of mixing are described only qualitatively (e.g., no mixing, moderate mixing, rapid mixing).

The objectives of this study were to (1) investigate the initial rate of adsorption of an HOC to an inorganic surface as a function of chemical (e.g., pH, ionic strength, presence of bivalent cations) and physical (e.g., relative mixing rate) parameters, (2) examine the rate of desorption of the HOC from the inorganic surface, and (3) determine the effects of aqueous chemistry on the amount of HOC adsorbed to the mineral surface at equilibrium. A primary goal was to elucidate the

role of a mineral surface in the adsorption process. For example, Schwarzenbach and Westall (1981) and Murphy et al. (1990) observed that the type of mineral was important in the adsorption of HOC in their studies, while Keoleian and Curl (1989) and Backhus (1990) both found that differences in HOC sorption between the sorbents they studied could be explained solely by differences in surface area.

Several techniques have been used previously to study the adsorption of HOC to inorganic surfaces. All of these methods, however, have relied on separating the solid sorbent phase from the aqueous phase (typically by centrifugation) to quantify the amount of pollutant associated with the sorbent. Inability to completely separate phases has resulted in observations of a "solids effect" in some adsorption studies (e.g., O'Conner and Connolly, 1980; DiToro and Horzempa, 1982) in which the measured adsorption constant decreases with increasing solids concentration. This separation problem has been recognized previously as the cause for observed solids effects (Gschwend and Wu, 1985; Morel and Gschwend, 1987; Voice et al., 1983; Voice and Weber, 1985). Therefore, methods capable of measuring concentrations in situ are ideal because separation difficulties may introduce artifacts in the determination of adsorption constants.

Perylene was the probe chosen to model hydrophobic organic pollutants. This nonpolar, nonionogenic PAH compound was selected in order to eliminate or minimize possible adsorption mechanisms other than the effects of the hydrophobic interaction in the sorption reaction, as described earlier. Also, the very hydrophobic compound perylene ($\log K_{ow} > 6$) was expected to show appreciable adsorption to

the inorganic surface utilized in this study. Because PAH compounds fluoresce in aqueous solution, probe concentrations can be determined by the inherently sensitive technique of fluorescence. PAH compounds have been used previously as models for nonionic, nonpolar HOC (e.g., Karickhoff et al., 1979; Backhus, 1990; Murphy et al., 1990; Backhus and Gschwend, 1990).

The model for mineral surfaces used in this study was the interior walls of fused silica fluorescence cells utilized in determining perylene concentrations. The bases for choosing this inorganic surface were threefold: (1) the applicability of fused silica as a model mineral surface with well-known surface characteristics, (2) the ability to measure the extent of adsorption without having to separate the solid and aqueous phases, and (3) the ability to measure the rates of adsorption on short time-scales (i.e., minutes) which has not been previously reported.

Contrary to two reported studies (Shimizu and Liljestrand, 1991; Liljestrand and Shimizu, 1991), the adsorption of PAH compounds to bare mineral surfaces does not result in the static quenching of PAH fluorescence. For example, the use of inorganic materials as substrates for studying the photochemistry of adsorbed organic molecules, as well as the use of fluorescent organic molecules to probe the solid-liquid interfacial region of inorganic colloids, has been extensively documented (Kalyanasundaram, 1987). Decreases in the fluorescence of PAH compounds upon adsorption to mineral surfaces results because of the removal of the fluorescing species from aqueous solution and/or the path of fluorescence detection.

For example, Backhus and Gschwend (1990) observed decreases in solution fluorescence intensities as perylene was adsorbing to their glassware during an experiment. In their case, perylene was being lost from solution to the walls of the experimental vessels before the transfer of samples to fluorescence cells for measurements. The present study used fluorescence cells both as reaction vessels and for measuring perylene concentrations in solution. The observed decreases in fluorescence resulted from removal of perylene (still fluorescent) from the path of the excitation source and/or from the view of the detector. The decreases in intensity were observed because of the particular geometry of the spectrofluorophotometer, not because the silica surface quenched the perylene fluorescence.

EXPERIMENTAL

Apparatus. Fluorescence measurements were made on a Shimadzu Model RF-540 Recording Spectrofluorophotometer with a right angle geometric sample chamber configuration. The excitation source was a 150W xenon-arc lamp and excitation and emission wavelengths were obtained with off-plane concave diffraction grating (900 lines/mm) monochromators. Fluorescence measurements for perylene and rhodamine 110 were made at the excitation/emission wavelengths of 432/470 and 496/520 nm, respectively, with slits set for bandwidths of 10 nm on both the excitation and emission monochromators.

Absorbance measurements were made on a Hewlett Packard 8451A Diode Array Spectrophotometer at the appropriate wavelengths to correct for the inner-filter effect. The spectral bandwidth was fixed at 2 nm. The spectrophotometer was equipped with a Hewlett Packard 89055A cell stirring module to allow mixing in the cells.

Fused silica fluorescence cells (Spectrosil, Starna Cells Inc.) with Teflon stoppers were used for both fluorescence and absorbance measurements. Fused silica cells contribute very little background fluorescence relative to quartz cells and are generally recommended for fluorescence work. The cells had a path length of 10 mm.

The pH of all aqueous solutions was measured with a Radiometer Model PHM84 Research pH Meter using a Radiometer GK2401C glass combination electrode. The pH meter was calibrated with NBS buffers.

Materials. The nonionic, nonpolar hydrophobic probe used in this study was perylene (Aldrich, 99+% pure). Relevant chemical and physical properties of perylene are listed in Table I. The conservative probe, rhodamine 110 (Lasergrade), was obtained from Kodak. Both were used without further purification.

A concentrated stock solution of rhodamine 110 (2.7 g/L, 7.4 mM) was prepared in methanol (Fisher, Spectroanalyzed). Because of its relatively low solubility in methanol, perylene was first dissolved in chloroform (J.T. Baker, Photrex) and an aliquot of this solution (120 mg/L, 475.6 μM) was then spiked into methanol to obtain the desired stock concentration. Finally, an aliquot of the concentrated stock of rhodamine 110 was spiked into the perylene stock to obtain the final working stock solution (120 μg/L (475.6 nM) perylene, 30 μg/L (81.8 nM) rhodamine 110 in methanol with 0.1% (v/v) chloroform). This solution was stored in the dark at 4°C in an amber borosilicate glass bottle to prevent photodegradation and/or volatilization. Aliquots of the solution were allowed to equilibrate (in the dark) at room temperature for at least 24 hours before use in the experiments.

All other reagents not specifically referred to were of analytical grade or better and were used without further treatment. All aqueous stock solutions were filtered through 0.2 μm pore polycarbonate Nuclepore filters prior to use.

Procedure. (A) General. Aqueous solutions were prepared with distilled, deionized water (D_2H_2O) (Corning Mega-Pure™ System). All experiments were performed at room temperature (23° C) in an open system (i.e., aqueous solutions were equilibrated with the surrounding atmosphere). The open system is a model

Table I. Chemical and Physical Properties of Perylene.

Structure	
Formula	$C_{20}H_{12}$
FW (g/mol)	252.32
Solid Density (g/cm^3)	1.35
mp (°C)[a]	277-279
ϕ_F [b]	~1.0
Molecular Length [c] (Å)	10.5
Total Surface Area [d] ($Å^2$)	251.5
Molar Volume [e] (mL)	202
log K_{ow} (M/M) [d]	6.50
distilled water solubility [f] (μg/L) (nM)	0.4 1.585
γ_i^{w} [g]	(x 10^{-7})
Distilled Water	8.721
0.001 M NaCl	8.727
0.01 M NaCl	8.793
0.1 M NaCl	9.461

[a]Supplied by Aldrich. [b]Quantum yield in aqueous solution [25°C] (Turro, 1978). [c]Estimated for major-axis from data of Klevins (1950). [d]Yalkowsky and Valvani (1979). [e]Estimated from correlation with solid density using data of Davis and Gottlieb (1962). [f]MacKay and Shiu (1977). [g]Calculated in Chapter 2.

which approximates the carbonate system of natural waters by equilibrating water with the atmosphere containing $CO_{2\,(g)}$ at a constant partial pressure (Stumm and Morgan, 1981). For waters which are in equilibrium with the atmosphere, the huge reservoir of $CO_{2\,(g)}$ imparts a significant buffering action above pH 7.

Fluorescence cells were cleaned by repeated soaking and rinsing, first with methanol and then D_2H_2O. Cell cleanliness was monitored with fluorescence and absorbance measurements. All other glassware was cleaned by soaking in either 4 M HNO_3 or 4 M HCl, rinsing repeatedly with D_2H_2O, and drying in an oven at 110° C.

Absorbance spectra were taken to determine the possible wavelengths which could be used for excitation of perylene and rhodamine 110. Fluorescence emission spectra were obtained by exciting the compounds at the wavelength of an absorption band in order to determine wavelengths at which fluorescence could be observed. The fluorescence emission spectrum of a pure substance is independent of the wavelength of excitation (Parker, 1968). Finally, fluorescence excitation spectra were recorded and an appropriate pair of excitation/emission wavelengths were selected for each compound. Wavelength pairs were chosen to maximize the fluorescence intensity and minimize the background interference (e.g., from co-solute interference and/or the Raman scattering of water).

(B) Long-Term Adsorption/Desorption Studies. Sample solutions were prepared by adding appropriate amounts of concentrated salt solution(s) to D_2H_2O in Erlenmeyer flasks and adjusting the pH with 0.1 M HCl and/or 0.1 M NaOH. The

samples were stirred until no further pH change was observed, indicating that they had equilibrated with the atmosphere.

A typical experiment consisted of pipetting 3 mL of a sample of known pH and ionic strength into a fluorescence cell containing a Teflon-coated micro stir bar (7 mm x 2 mm, Spinbar) and recording the fluorescence intensities at the appropriate wavelengths. The sample was then spiked with 10 μL of the combined perylene-rhodamine 110 stock solution and was immediately placed in the stirring module of the spectrophotometer. While mixing, the lid to the sample compartment was closed to prevent photodegradation. After an appropriate time for complete mixing in the cell (generally 1.5 minutes), the cell was placed in the spectrofluorophotometer and a fluorescence measurement for perylene was made. The sample was then returned to the spectrophotometer for further mixing and the procedure was repeated until no further change in perylene fluorescence was observed. The stirring rate for all of the long-term studies was qualitatively described as rapid mixing. When the rate of change of perylene fluorescence intensity decreased sufficiently (after 20 minutes), fluorescence measurements were made for rhodamine 110 as well. No absorbance measurements were necessary because the inner-filter effect was insignificant for these samples.

The initial perylene concentration of the samples after spiking was nominally 0.4 μg/L (1.6 n$\underline{M}$) while the rhodamine 110 concentration was nominally 0.1 μg/L (0.27 n$\underline{M}$). If comparisons between the samples were necessary, the perylene fluorescence intensities were first normalized by the mean of the rhodamine 110

fluorescence intensities in order to account for the slight variation in spiking volume between the different samples.

When no further change in perylene fluorescence was observed, the solution in the fluorescence cell was carefully drawn from the cell with a clean borosilicate glass Pasteur pipet. Another 3 mL of fresh sample of the same pH and ionic strength was then immediately pipetted into the fluorescence cell in order to desorb perylene from the cell walls. The sample was stirred and fluorescence measurements were recorded as before for the adsorption study. When no further change in fluorescence was detected, the solution was again drawn from the cell and the desorption step was either repeated or 3 mL of methanol was added with a Class A Pyrex volumetric pipet in order to extract the perylene from the cell walls.

(C) Short-Term Adsorption Studies. The adsorption of perylene to the inorganic silica surface of fluorescence cells over shorter time periods (40 minutes) was studied in the presence and absence of humic materials following a procedure adapted from Backhus and Gschwend (1990). The procedure enables the kinetics of perylene partitioning to humic material to be separated from the kinetics of perylene adsorption to the inorganic surfaces. Different relative rates of mixing (rapid, moderate, none) were utilized to investigate the importance of stirring in the cells. The short-term adsorption studies were otherwise similar to the long-term studies; a more complete description of the short-term procedure is detailed in Chapters 2 and 4.

Data Treatment. (A) Short-Term Adsorption of Perylene to Silica. The adsorption of nonionic, nonpolar HOC by inorganic surfaces was modeled on short time-scales by Backhus and Gschwend (1990) as a first-order, reversible rate process:

$$PAH_d \rightleftharpoons PAH\text{-}wall \tag{5.1}$$

where PAH_d is the dissolved PAH solute in the sample and PAH-wall is the PAH associated with mineral surfaces. Because the fluorescence intensity is proportional to $[PAH_d]$, the rate of adsorption of PAH by inorganic surfaces (i.e., loss of PAH_d from solution) can be monitored with fluorescence. For the initial condition $[PAH_d] = [PAH_T]$, where $[PAH_T]$ is the total PAH concentration (i.e., $[PAH_T]$ equals $[PAH_d]$ + [PAH-wall]), Backhus and Gschwend (1990) derived the following equation to describe the observed fluorescence versus time:

$$F = \frac{k_{-w} F_0}{k_w + k_{-w}} + \frac{k_w F_0}{k_w + k_{-w}} \exp[-(k_w + k_{-w})t] \tag{5.2}$$

where F_0 is the fluorescence at time zero and k_w and k_{-w} are the first-order forward and reverse rate constants for adsorption to the surfaces. Equation (5.2) is of the form:

$$F = B + Me^{-t/\tau} \tag{5.3}$$

where B is the PAH_d fluorescence at equilibrium and $M = F_0 - B$, a measure of the

PAH adsorbed. The reciprocal of the time constant, τ, is the sum of k_w and k_{-w}.

The reaction in equation (5.1) can be described equally well assuming a mass transfer process:

$$\frac{d[PAH_d]}{dt} = -\alpha([PAH_d] - [PAH_d]_{eq}) \qquad (5.4)$$

where α is a mass transfer coefficient and the subscript "eq" denotes the equilibrium measurement. Solving equation (5.4) gives a solution equivalent to equation (5.3), but the reciprocal of τ is now the mass transfer coefficient, α. For either description of perylene adsorption to fluorescence cell walls, a reaction quotient can be calculated from the fluorescence data and equation (5.3):

$$Q_w = \frac{[PAH\text{-}wall]}{[PAH_d](SA/V)} = \frac{M}{B(SA/V)} \qquad (5.5)$$

where (SA/V) is the surface area-to-volume ratio. In this context, Q_w (mL/cm^2) is an adsorption measurement prior to equilibrium (Stumm and Morgan, 1981). For the purposes of this study, (SA/V) was estimated from the geometry of the fluorescence cells. For relatively nonporous mineral surfaces, this estimation of (SA/V) should be equivalent to that which would be measured using BET $N_{2\,(g)}$ (e.g., see Chapter 3).

(B) Long-Term Adsorption/Desorption of Perylene to Silica. For the long-term adsorption studies which closely approached equilibrium, it was observed that equation (5.3) could not adequately fit the fluorescence data. Over long time periods,

there appeared to be two time constants which defined the adsorption process. Karickhoff (1980, 1984) has proposed a two-stage kinetic model to describe the sorption of HOC by sediments. The model is based on the assumption that two types of surface sites exist with which HOC solute molecules can associate. Assuming first-order processes, the adsorption of a PAH can be written:

$$PAH_d \overset{fast}{\rightleftharpoons} PAH\text{-}wall_1 \overset{slow}{\rightleftharpoons} PAH\text{-}wall_2 \tag{5.6}$$

where the subscripts 1 and 2 designate the different sites. A solution describing the kinetics of adsorption for equation (5.6) is of the form:

$$F = B + M_1 e^{-t/\tau_1} + M_2 e^{-t/\tau_2} \tag{5.7}$$

The two-stage kinetic model is capable of fitting either the adsorption or desorption of a sorbing solute. As for the case with the reaction in equation (5.1), the reaction in equation (5.6) can be described in an equivalent fashion mathematically as a series of mass transfer processes (Curtis et al., 1986a). For either case, the equilibrium adsorption constant, K_w^{eq} (mL/cm^2), can be written:

$$K_w^{eq} = \frac{[PAH\text{-}wall_1] + [PAH\text{-}wall_2]}{[PAH_d](SA/V)} = \frac{M_1 + M_2}{B(SA/V)} \tag{5.8}$$

RESULTS AND DISCUSSION

Short-Term Adsorption Studies. (A) Aqueous Chemistry Effects. The adsorption of perylene to the fused silica surface of fluorescence cells over short time periods (40 minutes) was studied in the presence and absence of natural organic material (NOM). For all short-term experiments investigating the effect of aqueous chemistry, the rate of mixing was qualitatively characterized as moderate. A complete description of the procedure used for the short-term adsorption studies is detailed in Chapters 2 and 4. The procedure enables the kinetics of perylene partitioning to NOM to be separated from the kinetics of perylene adsorption to bare mineral surfaces (Backhus and Gschwend, 1990; this work, Chapters 2 and 4).

In the presence and absence of NOM, measurements of the perylene fluorescence intensity decreased exponentially with time (Figure 1). The distinct and parallel curves obtained for various concentrations of NOM indicate that the binding of perylene by NOM is very fast relative to the adsorption of perylene by the silica surface and that the two reactions are relatively independent of each other. In other words, the presence of the inorganic surface does not interfere with the NOM binding reaction and the presence of NOM does not affect the subsequent adsorption of perylene to silica. The presence of NOM in the system only changes the initial $[PAH_d]$ (i.e., the initial amount of perylene available to be adsorbed at the silica surface). In effect, samples with varying NOM concentrations are analogous to data points in an isotherm experiment with regard to the amount of perylene adsorbed at a silica surface versus the concentration of perylene remaining in solution.

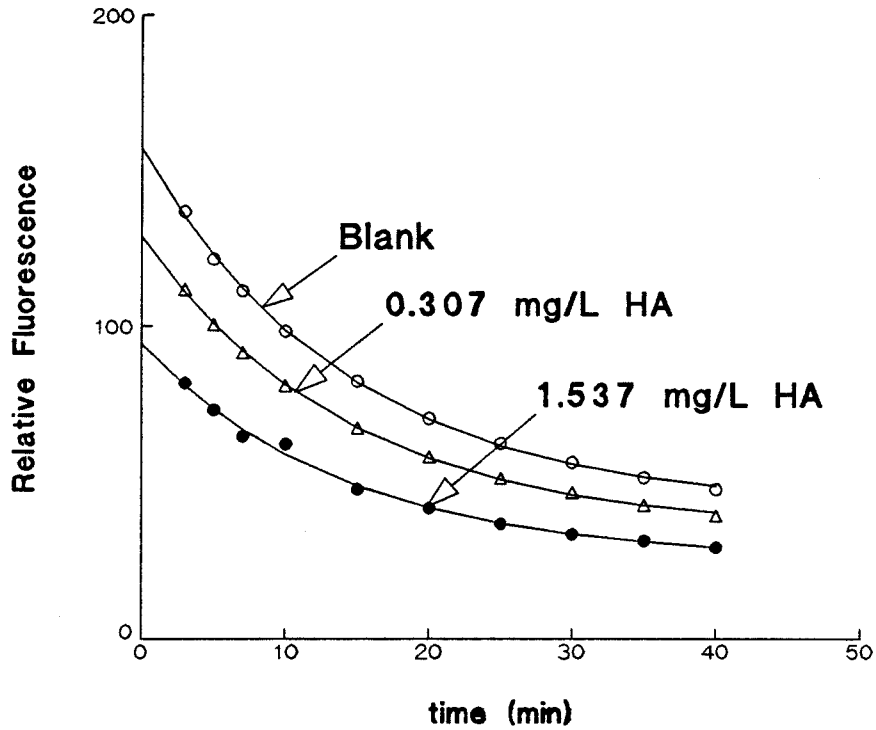

Figure 1. Adsorption of perylene to fused silica fluorescence cell walls versus time in the presence and absence of dissolved humic acid in 0.1 M NaCl solutions at pH 4. Nominal perylene concentration for each sample was 0.4 μg/L (1.6 nM). Moderate mixing conditions were utilized.

A nonlinear least-squares curve-fitting program was used to fit equation (5.3) to the measured fluorescence intensities of all the samples spiked with perylene, and the parameters B, M and τ were determined. A reaction quotient, Q_w, was determined for each sample using equation (5.5). Average values of τ and Q_w were calculated for the samples having similar aqueous chemistry conditions and are listed in Table II.

The effects of aqueous chemistry on the short-term adsorption of perylene by the silica surface of fluorescence cells can be seen in Figure 2. At constant ionic strength, values of Q_w decreased with an increase in pH for all samples, both in the presence and absence of Ca^{2+} (Figure 2a). In NaCl solutions, increases in the electrolyte concentration resulted in an increase in Q_w for samples at pH 4 and 7, while the opposite trend was observed at pH 10. The presence of 1 mM Ca^{2+} (0.1 M total ionic strength) had little effect on Q_w at pH 4 relative to monovalent salt solutions. At pH 7 and 10, however, the presence of Ca^{2+} increased the adsorption significantly relative to the NaCl solutions of similar total ionic strength.

An alternative means of characterizing the adsorption of perylene to inorganic surfaces on short time-scales is to examine τ, the time constant or characteristic time for the initial adsorption reaction. In Figure 2b, for example, it is observed that the characteristic time for adsorption increased with increasing pH for all samples of similar salt content. The time constant increased with ionic strength for NaCl solutions at pH 10, whereas a barely perceptible increase at pH 7 and a decrease at pH 4 is observed for τ with increasing NaCl concentrations. The effect of Ca^{2+} on

Table II. Aqueous Chemistry Effects on Short-Term Adsorption.[a,b]

	Q_w [c] (mL/cm^2)	τ (min)	α [d] (hr^{-1})
pH 4			
0.001M NaCl	0.347 ± 0.088 (12)	14.24 ± 2.94 (13)	4.21
0.01M NaCl	0.488 ± 0.110 (13)	13.63 ± 1.85 (12)	4.40
0.1M NaCl	0.487 ± 0.109 (13)	12.46 ± 2.19 (12)	4.82
1 mM Ca^{2+} [e]	0.488 ± 0.121 (13)	12.41 ± 2.27 (13)	4.83
pH 7			
0.001M NaCl	0.295 ± 0.091 (12)	14.85 ± 1.55 (13)	4.04
0.01M NaCl	0.388 ± 0.093 (12)	15.00 ± 1.21 (11)	4.00
0.1M NaCl	0.384 ± 0.089 (13)	15.21 ± 1.52 (13)	3.94
1 mM Ca^{2+} [e]	0.482 ± 0.088 (13)	13.72 ± 1.73 (13)	4.37
pH 10			
0.001M NaCl	0.294 ± 0.063 (13)	17.94 ± 3.60 (11)	3.34
0.01M NaCl	0.239 ± 0.043 (12)	18.87 ± 1.18 (11)	3.18
0.1M NaCl	0.202 ± 0.018 (10)	20.17 ± 2.43 (12)	2.97
1 mM Ca^{2+} [e]	0.314 ± 0.031 (10)	17.10 ± 1.83 (10)	3.51

[a] Moderate mixing. [b] Values are reported ± one standard deviation for the number of samples in parentheses. [c] Calculated using equation (5.5). SA/V = 4.333 cm^2/mL. [d] $1/\tau$. [e] 0.1 M total ionic strength.

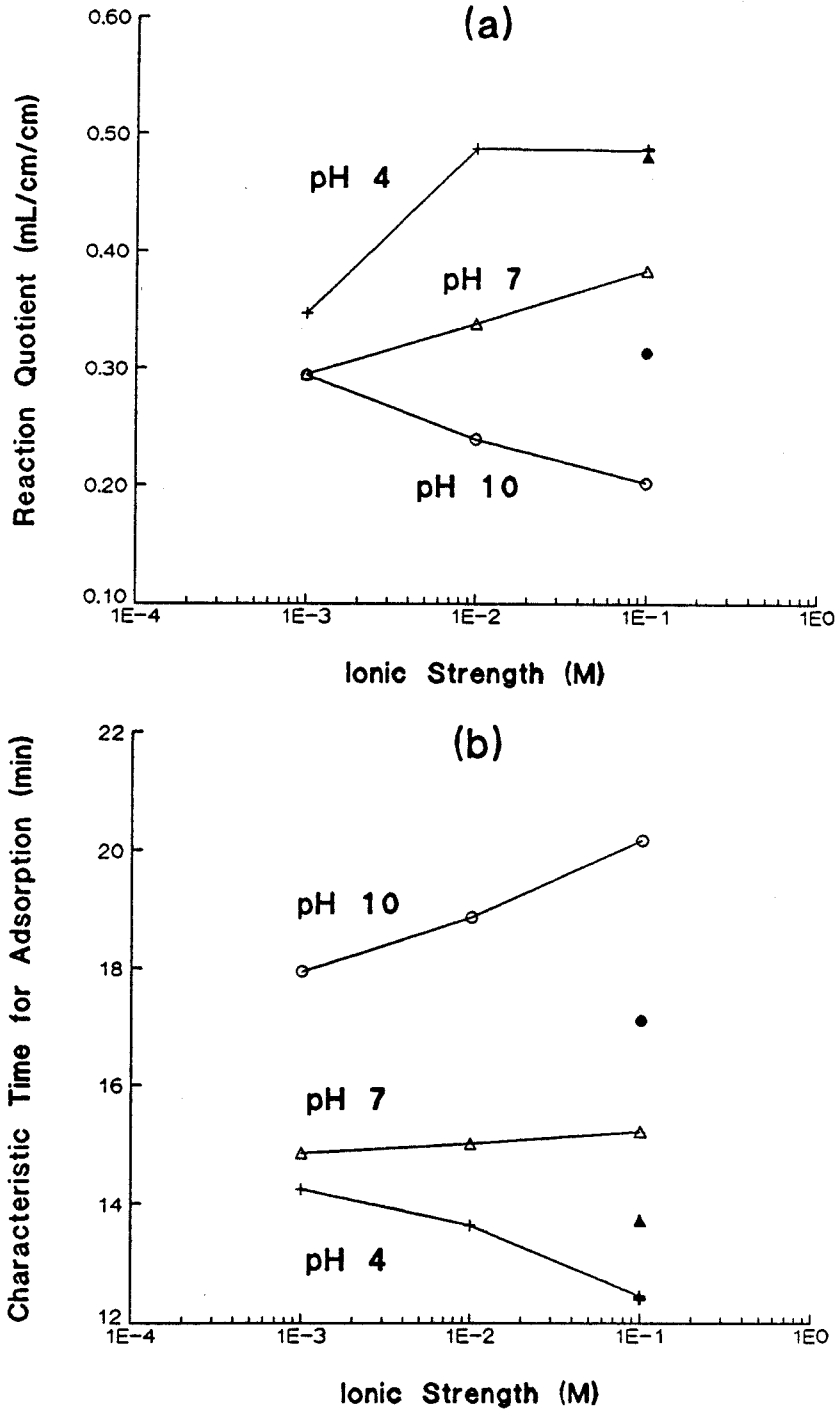

Figure 2. Effects of solution chemistry on the short-term adsorption of perylene by fused silica. Symbols connected by lines refer to NaCl samples. Single (**bold**) points at a total ionic strength of 0.1 M refer to experiments with 1 mM Ca^{2+} at the appropriate pH values. Moderate mixing was used for all samples. a) Reaction quotient versus ionic strength. b) Characteristic time constant versus ionic strength.

the time constant was opposite to that observed for Q_w; at pH 7 and 10 it caused a decrease in τ relative to NaCl solutions, but again had little effect at pH 4.

(B) Rate of Mixing. The effect of different stirring rates on the short-term adsorption of perylene by the fluorescence cell walls was examined for three conditions: no mixing, moderate mixing and rapid mixing. Mixing effects were investigated at pH 4 for varying NaCl concentrations. The results for the reaction quotient and the characteristic time for adsorption are listed in Table III.

A significant effect on Q_w was observed for the different stirring rates as shown in Figure 3a. Although more vigorous mixing increased the value of Q_w for all NaCl concentrations, the increase in Q_w was smaller between the moderately- and rapidly-mixed samples than it was between samples without mixing and with moderate mixing. When a constant rate of mixing was maintained, increases in the ionic strength caused minor increases in Q_w, but the magnitude of the effect was not nearly as large as that observed for varying stirring rates.

Mixing rates also affected the characteristic time for initial adsorption (Figure 3b). Increases in the rate of stirring decreased τ for all samples of equivalent electrolyte concentration, and again a greater difference was observed between the samples without mixing and with moderate mixing than was observed between the moderately- and rapidly-mixed samples. For similar mixing conditions, increases in the ionic strength generally caused decreases in τ, but again the magnitude of the effect was smaller than that for varying mixing rates.

Table III. Effect of Mixing on Short-Term Adsorption.[a,b]

	Q_w [c] (mL/cm^2)	τ (min)	α [d] (hr^{-1})
Rapid Mixing			
0.001M NaCl	0.591 ± 0.062 (13)	12.68 ± 2.09 (14)	4.73
0.01M NaCl	0.587 ± 0.079 (13)	12.89 ± 2.09 (13)	4.65
0.1M NaCl	0.645 ± 0.125 (13)	12.18 ± 2.32 (10)	4.93
Moderate Mixing			
0.001M NaCl	0.347 ± 0.088 (12)	14.24 ± 2.94 (13)	4.21
0.01M NaCl	0.488 ± 0.110 (13)	13.63 ± 1.85 (12)	4.40
0.1M NaCl	0.487 ± 0.109 (13)	12.46 ± 2.19 (12)	4.82
No Mixing			
0.001M NaCl	0.060 ± 0.011 (10)	20.14 ± 4.44 (12)	2.98
0.01M NaCl	0.098 ± 0.042 (13)	15.01 ± 1.34 (10)	4.00
0.1M NaCl	0.077 ± 0.040 (15)	15.75 ± 3.61 (14)	3.81

[a] pH 4. [b] Values are reported ± one standard deviation for the number of samples in parentheses. [c] Calculated using equation (5.5). SA/V = 4.333 cm^2/mL. [d] $1/\tau$.

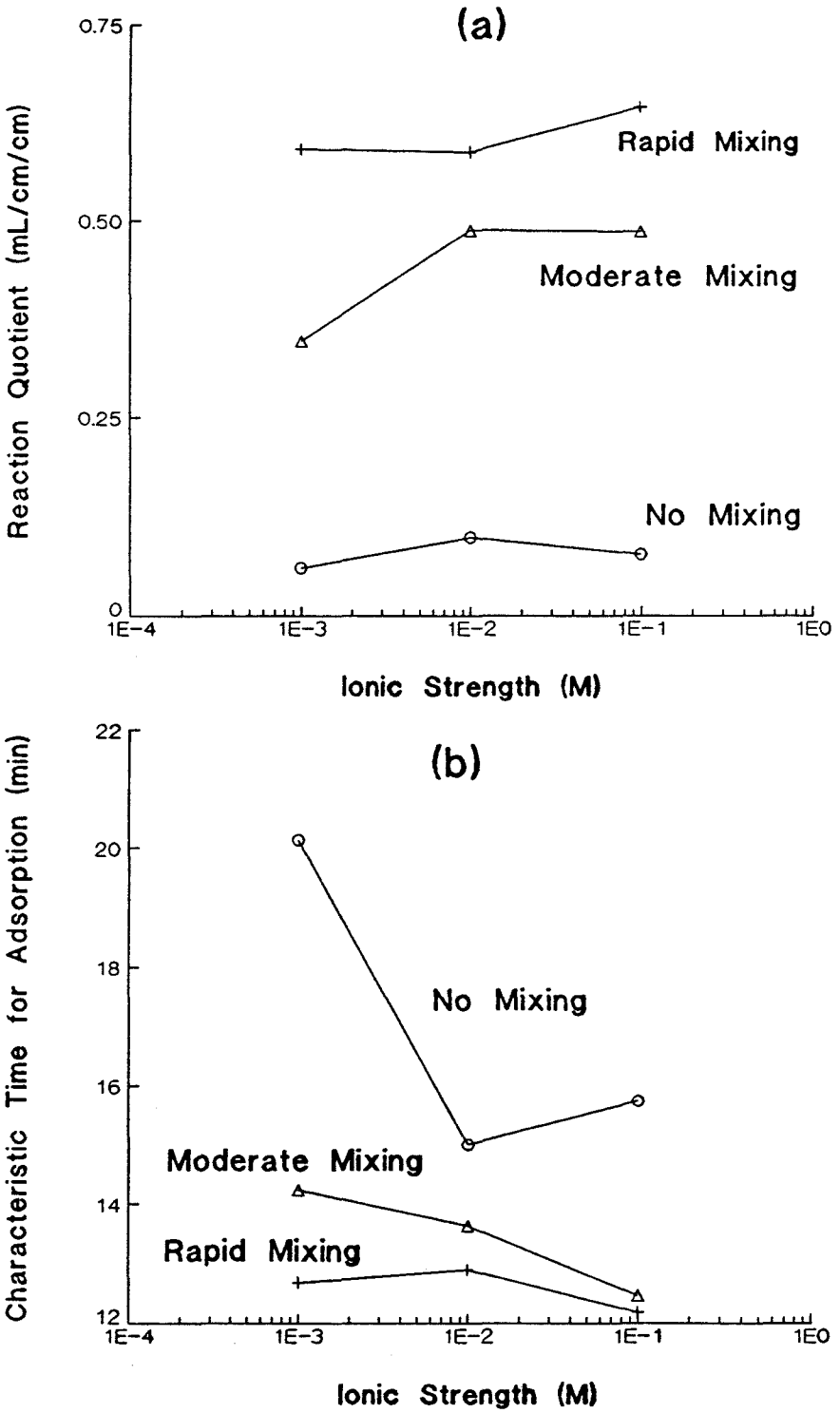

Figure 3. Effect of mixing on the short-term adsorption of perylene by fused silica. All data are for NaCl samples at pH 4. a) Reaction quotient versus ionic strength. b) Characteristic time constant versus ionic strength.

These results agree with the observations of Backhus (1990). She examined the adsorption of perylene to glass walls both with and without shaking the samples on a wrist-action shaker and observed that equilibrium was attained faster with shaking than without. The effect of mixing on the rate of adsorption can be explained by the stagnant film postulated to exist between a surface and a well-mixed solution. The rate of diffusion across the film depends upon the thickness of this surface stagnant layer. The magnitude of the thickness is determined by the mixing rate, because vigorous stirring reduces the stagnant layer thickness. Because the characteristic time for adsorption decreased when the mixing rate increased, a mass transfer step must contribute to the observed rates for the initial adsorption of perylene by the cell walls over short time periods. This contribution would be significant for samples without stirring, but would become less important as the rate of mixing increased.

Long-Term Adsorption Studies. The adsorption of perylene by the silica fluorescence cell walls was examined over longer time periods in a few experiments in order to determine adsorption constants corresponding to equilibrium conditions. All long-term experiments were performed at pH 4. Rapid mixing conditions were maintained in an attempt to minimize the contribution of mass transfer in the rate of adsorption as discussed above. Fluorescence data were fit using equation (5.7), and the parameters M_1, M_2, τ_1, τ_2, and B were determined. An equilibrium adsorption constant, K_w^{eq}, was calculated utilizing equation (5.8) and the fitted parameters.

The adsorption of perylene by the silica surface in 1 mM NaCl at pH 4 is shown in Figure 4 for two duplicate experiments, and the values of the fitting parameters are listed for the respective studies. The time required for equilibrium to be attained was ~2½ hours in these two experiments; the time required for equilibration of the other adsorption experiments ranged from 2½ to 4 hours. As shown in Figure 4, the observed decreases in perylene fluorescence intensity with time cannot be modeled adequately with a single exponential decay expression. The reproducibility of the experiments is observed to be relatively good for the rapid mixing conditions utilized in the duplicate experiments. This was expected to a certain degree, based on the data in Table III; the relative standard error for Q_w was observed to be consistently higher for samples having less vigorous mixing.

The results of all long-term adsorption studies are listed in Table IV. In contrast to the short-term adsorption results, there were no obvious trends with varying concentrations of NaCl. Likewise, the presence of 1 mM Ca^{2+} appeared to have little effect in these systems. The characteristic time for quick adsorption, τ_1, showed no significant correlation with ionic strength, while the time constant for the slower adsorption process, τ_2, showed a moderate positive correlation with ionic strength. The fraction of perylene that was adsorbed very quickly (i.e., with a characteristic time τ_1) showed only a weak positive correlation with salt concentration. The most surprising results from the long-term adsorption studies were the apparent insensitivity of K_w^{eq} to the ionic strength and the ~200% increase in

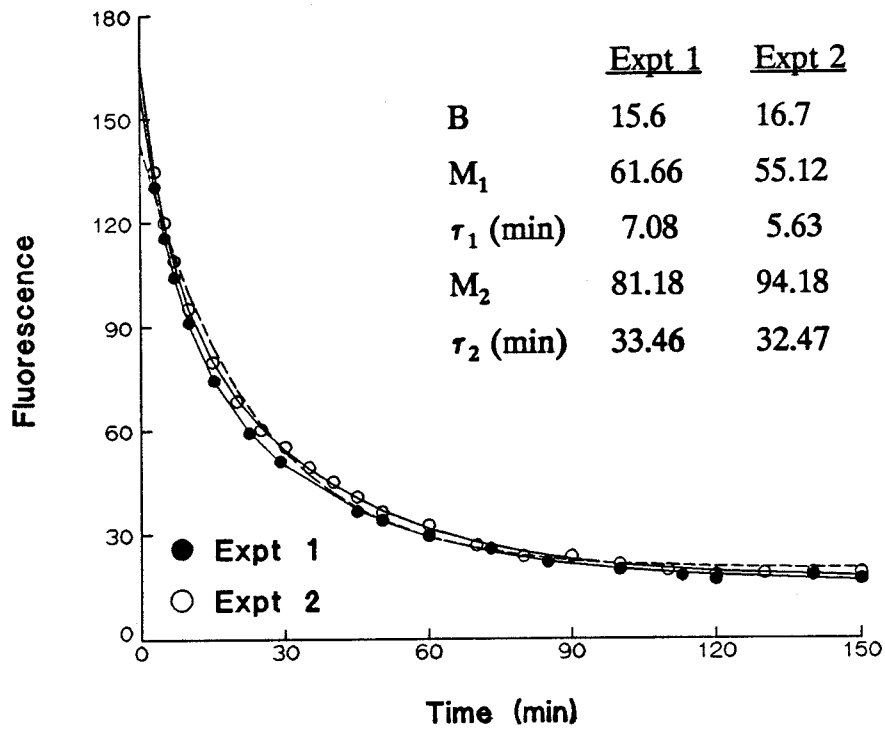

Figure 4. Long-term adsorption of perylene by fused silica in 0.001 M NaCl at pH 4 for duplicate experiments. Rapid mixing was used for both samples. The dashed line represents the best fit of Expt 2 data utilizing a single exponential decay expression [i.e., equation (5.3)]

Table IV. Long-Term Adsorption Results.[a]

	τ_1 (min)	τ_2 (min)	Fraction[b] Fast Adsorption	K_w^{eq} [c] (ml/cm^2)	Q_w [d,e] (ml/cm^2)	τ [e] (min)
0.001M NaCl						
Expt 1	7.08	33.46	43.2%	2.11,2.07*	0.834	14.76
Expt 2	5.63	32.47	36.9%	2.06	0.663	13.95
0.01 M NaCl						
Expt 3	4.89	31.67	41.6%	2.24	0.712	12.18
0.1 M NaCl						
Expt 4	6.92	39.21	45.6%	2.04	0.626	13.35
1 mM Ca^{2+} [f]						
Expt 5	6.31	44.34	51.0%	2.09	0.576	11.15

[a] pH 4, rapid mixing. [b] Calculated as $M_1/(M_1 + M_2)$. [c] Calculated using equation (5.8) except for the value denoted with an asterisk which was determined from the extracted mass. SA/V = 4.333 cm^2/mL. [d] Calculated using equation (5.5). SA/V = 4.333 cm^2/mL. [e] Determined for the first 40 minutes of fluorescence data. [f] 0.1 M total ionic strength.

K_w^{eq} relative to Q_w, the reaction quotient calculated from the first 40 minutes of data and using equation (5.5).

Caution must be used, however, in interpreting the results from these long-term adsorption studies because of the limited data that was obtained. More work, particularly in examining the effects of pH on the amount of adsorption at equilibrium, is needed in order to facilitate comparisons with the short-term data.

Desorption Studies. Desorption of perylene from the silica surface of fluorescence cells was investigated in order to compare the reaction rates with those observed in the long-term adsorption studies. The experimental conditions, therefore, were equivalent to those utilized in the long-term adsorption studies. The silica surface, which had been pre-equilibrated with perylene solutions, was exposed to fresh salt solutions of the same pH and ionic strength in order to facilitate desorption of the perylene. Fluorescence data from the desorption studies was fitted with equation (5.7) and the various parameters were determined for each experiment.

The results from a typical desorption experiment are shown in Figure 5, along with the optimized parameters obtained from the model fit. Again, it is apparent that the fluorescence data cannot be modeled with a single exponential equation. Data for all of the desorption studies are listed in Table V. In general, the characteristic times for desorption were significantly smaller than those observed in the adsorption studies. Also, the fraction of perylene that desorbed with a characteristic time τ_1 was generally less than the fraction of perylene which was adsorbed in the faster adsorption step. As for the long-term adsorption studies, there were no obvious

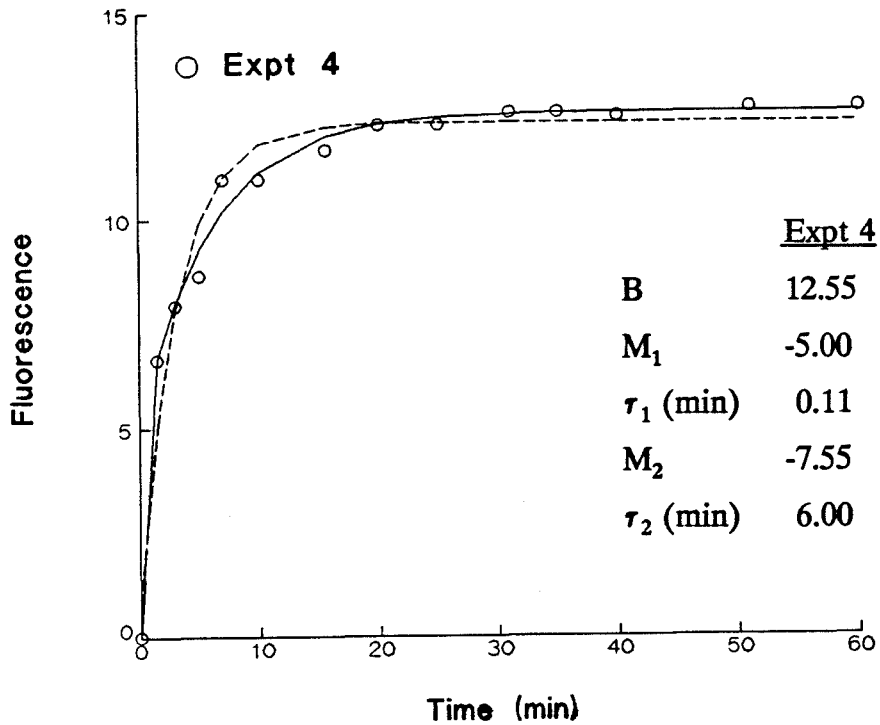

Figure 5. Desorption of perylene from fused silica in 0.1 M NaCl at pH 4. Rapid mixing conditions were maintained. The dashed line represents the best fit of Expt 4 data utilizing a single exponential decay expression [i.e., equation (5.3)]

Table V. Desorption Results.[a]

	τ_1 (min)	τ_2 (min)	Fraction[b] Fast Desorption	Extracted[c] Mass Recovery
0.001M NaCl				
Expt 1	ND[d]	ND	ND	99%
Expt 2[e]	0.42	7.06	28.3%	
	1.06	18.26	49.3%	88%
0.01 M NaCl				
Expt 3	1.37	13.85	27.5%	87%
0.1 M NaCl				
Expt 4	0.11	6.00	39.8%	95%
1 mM Ca^{2+}[f]				
Expt 5	0.14	11.78	37.5%	86%

[a] pH 4, rapid mixing. [b] Calculated as $M_1/(M_1 + M_2)$. [c] Calculated after methanol extraction as F_{MeOH}/F_{ads}. [d] ND, not determined. [e] Two consecutive desorption studies were performed in Expt 2. [f] 0.1 M total ionic strength.

trends in the desorption model parameters with varying ionic strength.

The desorption reactions were monitored until no further change in perylene fluorescence intensity was apparent; the time periods required for stabilization ranged from 60 to 90 minutes. It is uncertain, however, whether the desorption reactions were truly equilibrated after these time periods. For example, the adsorption constant which would be calculated at the end of the desorption study shown in Figure 5 is ~2.48 mL/cm^2. This constant is higher than 2.04 mL/cm^2, the value of K_w^{eq} calculated from the adsorption study (Table IV). It appears likely, therefore, that a relatively small fraction of perylene desorbs from the silica surface beyond the period of time examined in these studies and at a much slower rate than was observed here.

At the end of each experiment, the inorganic surface of the fluorescence cells was extracted with methanol and the adsorbed perylene concentrations were determined by fluorescence measurements. After the addition of methanol, the contents of the cells were stirred and fluorescence intensities were monitored with time. The perylene was completely extracted from the cell walls in 5 to 10 minutes for all of the experiments, as indicated by unchanging fluorescence measurements after these time periods.

From the extracted perylene concentrations, mass balance calculations were made and are listed in Table V as the fraction of adsorbed perylene (i.e., determined from the numerator in equation [5.8]) recovered by methanol extraction (i.e., direct measurement). Over 85% of the adsorbed perylene was recovered by methanol

extraction in all of the experiments. In particular, in the one experiment for which perylene was extracted directly after the adsorption study (Expt 1), almost all of the adsorbed perylene was recovered (Table V). The lower recoveries in the other experiments are believed to be artifacts resulting from the additional sample manipulations which were necessary for the desorption studies; for these experiments, any errors introduced in the manipulations are propagated throughout the study. An equilibrium adsorption constant was calculated for Experiment 1 utilizing the direct measurement of perylene adsorbed to the silica surface as determined by methanol extraction; this value compares very well with the other values of K_w^{eq} which were calculated using the total amount of perylene added and the final dissolved concentrations and inferring the amount sorbed by difference (Table IV).

The extraction of the cell walls with methanol and the recovery of perylene give a direct observation of the mass of perylene adsorbed to the inorganic surface. Without this information, the decay in fluorescence intensity with time (e.g., Figure 4) is only a measure of perylene being lost from solution. Because other processes may also deplete the concentration of perylene in the aqueous phase (e.g., volatilization, photodegradation, etc.), adsorption of perylene to inorganic surfaces can only be inferred in the absence of mass balance data.

Nature of HOC-Mineral Surface Interaction. The focus of this study was principally on the initial kinetics of the adsorption and desorption reactions between perylene and fused silica. From the results obtained in this study and from other studies, an attempt at understanding the mechanisms by which nonpolar, nonionic

HOC associate with inorganic surfaces can be made.

A principal hypothesis guiding this study was that the rate and extent of adsorption of HOC by a bare mineral surface should depend on the aqueous activity coefficient (γ_i^w) of the hydrophobic solute and on the relative hydrophobicity of the bare mineral surface. Any observed changes in the rate or extent of adsorption would therefore result because of a change in either one or both of these parameters.

In order to gain insight into the molecular-level adsorption mechanism, the effects of aqueous chemistry on HOC association with mineral surfaces must be understood. Changes in the aqueous chemistry can affect both HOC and mineral surface properties, as well as their interactions with water and each other. Examples of these changes are the "salting out" of HOC with increasing salinity and the protonation-deprotonation of surface hydroxyl groups in metal oxides. Because γ_i^w and the surface hydrophobicity of silica are both affected by aqueous chemistry conditions, interpretation of the effects of pH, ionic strength and the presence of Ca^{2+} on perylene adsorption by fused silica surfaces can be complicated.

The inorganic surfaces utilized in this study were the interior walls of fluorescence cells. In order to characterize the effects of solution chemistry on the silica surface, surface chemical reactions of the cell walls were modeled utilizing SURFEQL and equilibrium constants from Rea and Parks (1990). SURFEQL is a computer code adapted from MINEQL (Westall et al., 1976) to solve equilibrium surface speciation calculations (Faughnan, 1981). The model-dependent equilibrium constants from Rea and Parks (1990) are applicable for use with the triple layer

surface complexation model. The intrinsic equilibrium constants were originally determined for pyrogenic silica and were utilized (with slight modifications) by Rea and Parks (1990) to simulate inorganic ion adsorption on quartz. The pertinent reactions and corresponding equilibrium constants applicable to this study are shown in Table VI.

The surface speciation of fused silica for the solution chemistry conditions of this study is shown in Figure 6. As can be seen, the neutral surface hydroxyl groups dominate the distribution over the pH range of most natural waters, and the adsorption of metal cations becomes important only for neutral to high pH conditions. In NaCl solutions, the net charge on the silica surface is negative above approximately pH 2. In the presence of 1 m$\underline{M}$ Ca^{2+} (0.1 $\underline{M}$ total ionic strength), the net charge at the surface becomes positive above pH 4 because of the surface exchange reactions in which some bivalent cations replace protons at surface hydroxyl sites (Table VI, Figure 6d).

The effect of solution chemistry on HOC can be quantified with an aqueous activity coefficient; values of γ_i^w for perylene were calculated in Chapter 2 for the different solution conditions of this study. Briefly, the solubility of perylene in salt solutions was estimated using the Setschenow relationship and data from MacKay and Shiu (1977) for the solubility of perylene in distilled water. Values of γ_i^w were then calculated after correcting for the energy "cost" of melting the solid solute. The values of γ_i^w for perylene in varying salt solutions are listed in Table I.

Table VI. Reactions and Intrinsic Equilbrium Constants for Surface Ionization and Electrolyte Adsorption on Fused Silica.[a,b]

$SiOH_2^+ \rightleftharpoons SiOH + H^+$	$pK_{a1} = -3.2$
$SiOH \rightleftharpoons SiO^- + H^+$	$pK_{a2} = 7.2$
$Na^+ + SiOH \rightleftharpoons SiO\text{-}Na + H^+$	$p^*K_{Na+} = 6.7$
$Ca^{2+} + SiOH \rightleftharpoons SiO\text{-}Ca^+ + H^+$	$p^*K_{Ca2+} = 3.8$
$Ca^{2+} + H_2O + SiOH \rightleftharpoons SiO\text{-}CaOH + 2H^+$	$p^*K_{CaOH+} = 3.8$

$C_1 = 1.295\ F/m^2$

$C_2 = 0.2\ F/m^2$

$N_s = 5\ sites/nm^2$

[a] Constants from Rea and Parks (1990) are for use with a triple layer surface complexation model. [b] The formulas of surface complexes indicate the assumed location of constituents of the complex. The entire surface complex is located directly on the surface unless a dash is present in the formula. If a dash is present, everything to the left of the dash is located on the surface and everything to the right of the dash is located in the outer Helmholtz plane.

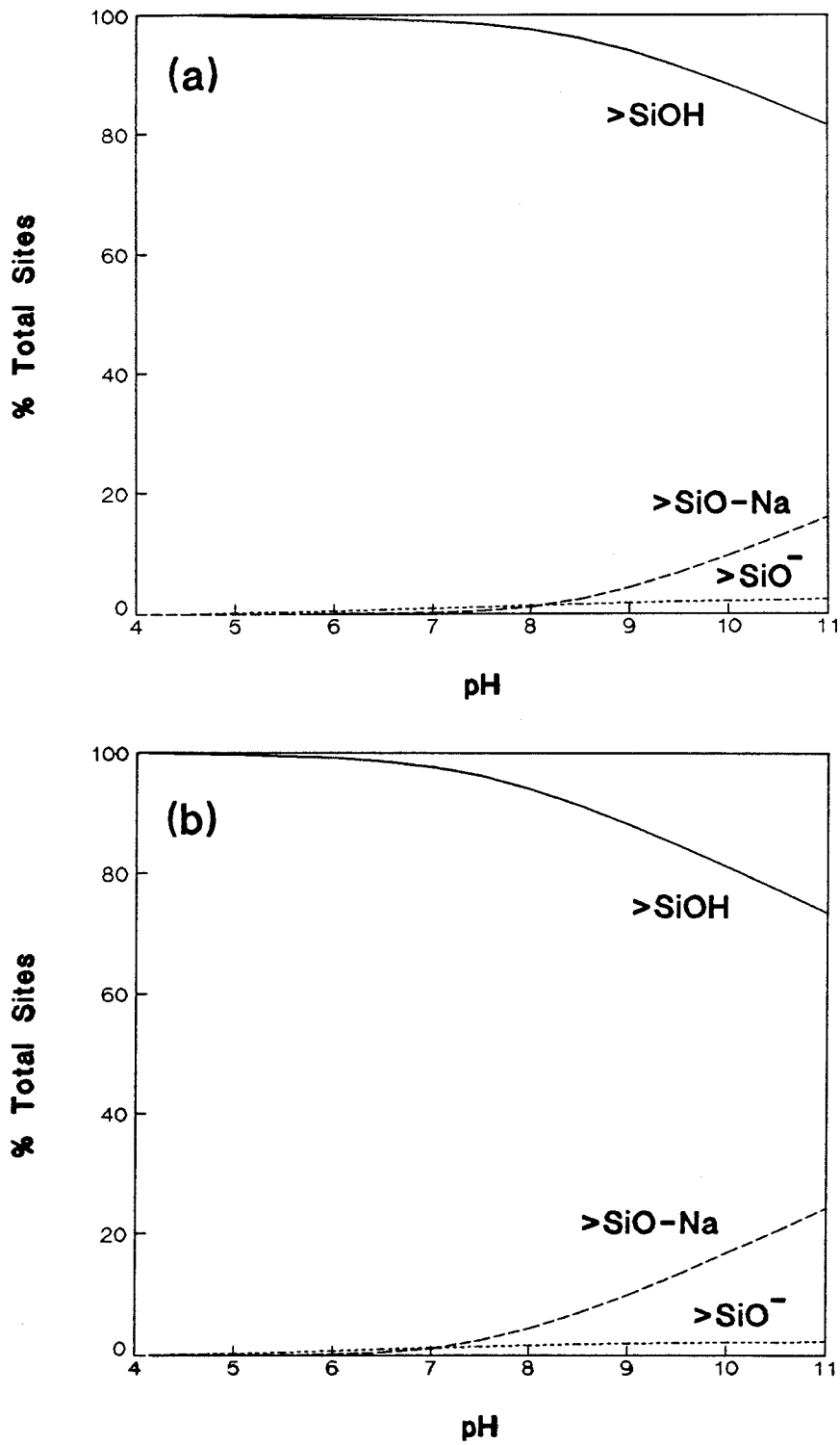

Figure 6. Surface speciation of fused silica from pH 4-11 using a triple layer model and the surface acidity and adsorption constants from Table VI. a) 0.001 M NaCl. b) 0.01 M NaCl.

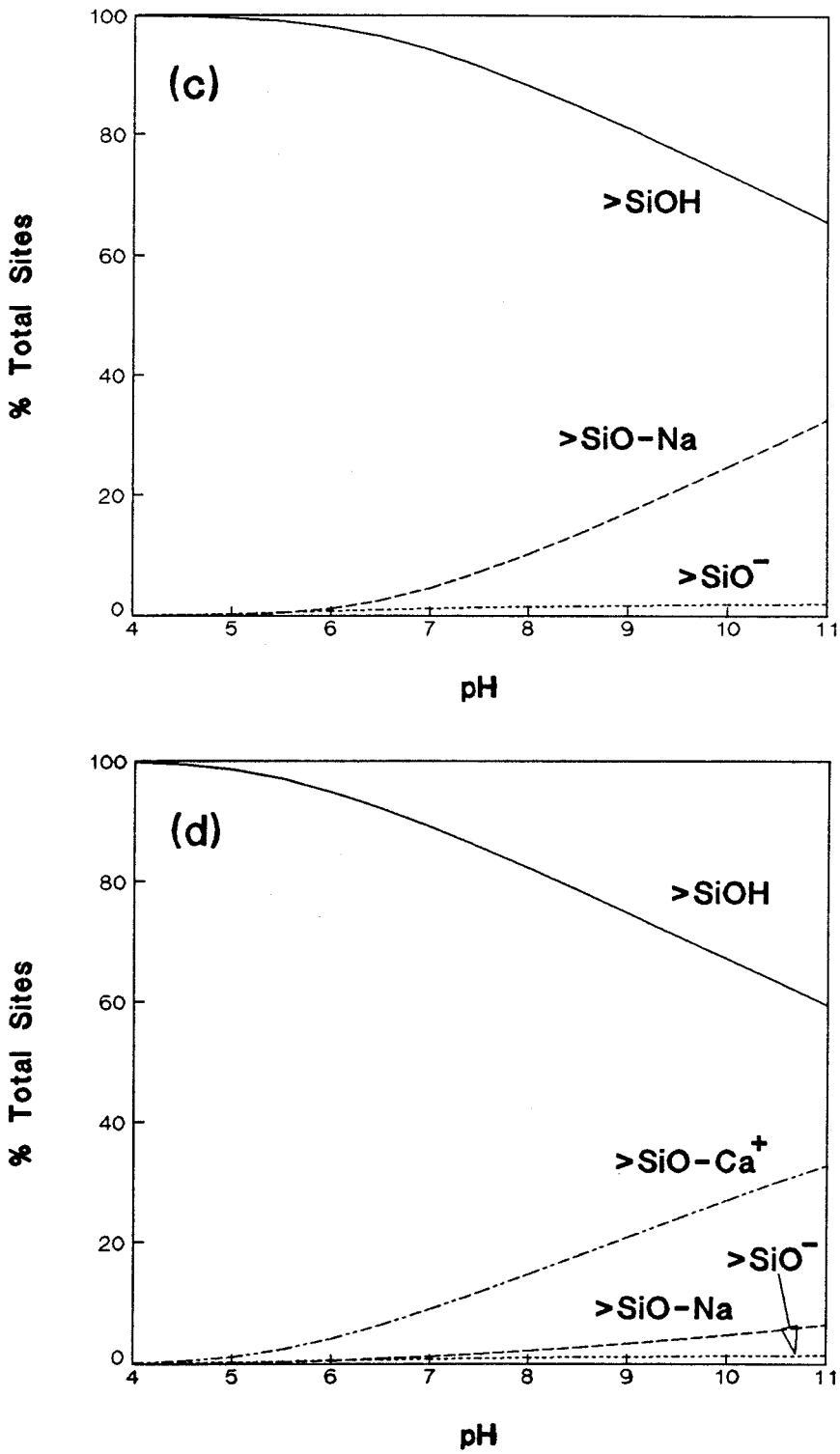

Figure 6. Surface speciation of fused silica from pH 4-11 using a triple layer model and the surface acidity and adsorption constants from Table VI. c) 0.1 M NaCl. d) 1 mM Ca^{2+} and 0.1 M total ionic strength.

By understanding how changes in aqueous chemistry affect the properties of the silica surface and dissolved perylene, an idea of the important processes driving the adsorption reaction can be obtained. In Figure 2 it was observed that the short-term adsorption of perylene on the silica surface was affected by the pH, ionic strength, and the presence of Ca^{2+}. The data in Figure 2 was presented in terms of a reaction quotient, Q_w, and also in terms of a characteristic time for initial adsorption, τ. In order to facilitate comparison between these two parameters, the reciprocal of τ can be calculated. This parameter, α, is typically thought of as a mass transfer coefficient as discussed previously. Because of the ill-defined roles of mass transfer and chemical reactions in this study, α is used here only as a measure of the initial rate of adsorption (e.g., an observed rate constant). Values of α were calculated and are listed in Tables II and III for the short-term adsorption experiments. Values of α versus ionic strength are shown in Figure 7 for the experiments in Table II. As might be expected, the plots of α and Q_w in Figures 2a and 7 have similar trends.

If the rate of perylene adsorption to an inorganic surface is dependent on the fugacity of the hydrophobic solute and the adsorption mechanism is not too complicated, an increase in γ_i^w should result in a faster rate of adsorption. Likewise, if a mineral surface is "hospitable" to a hydrophobic molecule, one might expect the rate of adsorption to depend on the degree of this characteristic. Because γ_i^w increases with increasing ionic strength (Table I), a concurrent increase in α would be expected for systems in which the energy driving adsorption results from solute

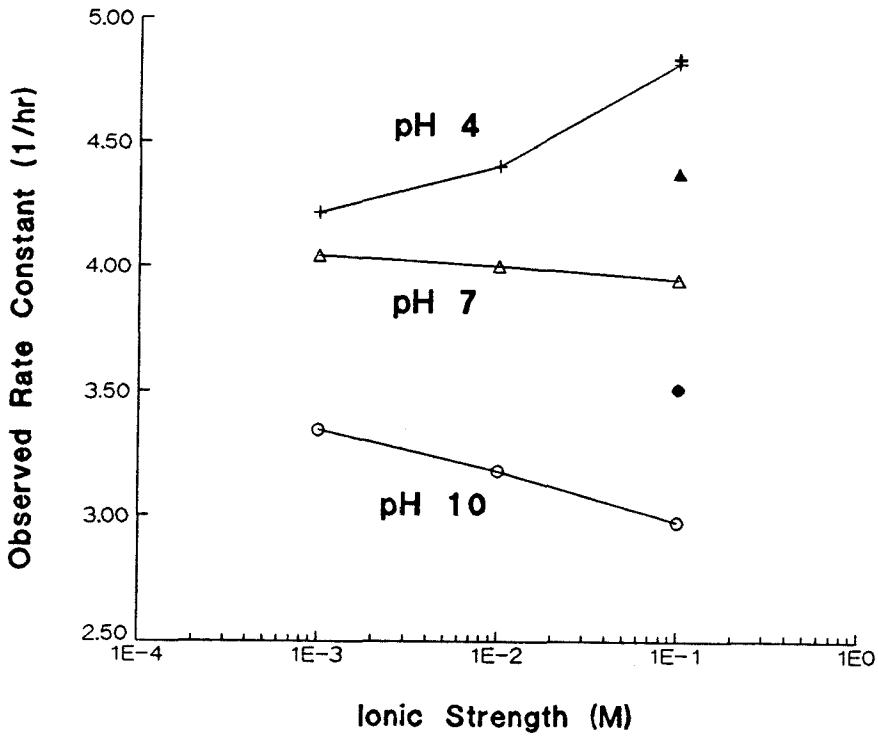

Figure 7. Effects of solution chemistry on the observed rate constant for perylene adsorption on fused silica. Symbols connected by lines refer to NaCl samples. Single (**bold**) points at a total ionic strength of 0.1 M refer to experiments with 1 mM Ca^{2+} at the appropriate pH values. Moderate mixing was used for all samples.

fugacity. This may explain the trend observed at pH 4 in Figure 7. Because very little charge is developed on the silica surface at pH 4, the surface charge density is relatively low (Figure 6). Regardless of the composition of the background electrolyte, essentially 100% of the sites are neutral hydroxyl groups.

A similar increase in α with increasing ionic strength is not observed in NaCl solutions at pH 7. Because changes in pH have little effect on γ_i^w in the samples of this study, a similar driving force to that exerted at pH 4 should be operative at pH 7; therefore, the surface properties would appear to be impeding the rate of adsorption somewhat at this pH value. In Figure 6, it is observed that increases in the NaCl concentration at pH 7 result in increasing amounts of Na^+ bound at the silica surface. At pH 10, the fraction of sites binding Na^+ becomes quite significant with increasing ionic strength. Not too surprisingly, a considerable decrease in α with increasing NaCl concentration at pH 10 is observed.

Trends between the silica surface speciation and rates of perylene adsorption can also be seen in the presence of Ca^{2+}. At pH 4, very little Ca^{2+} is associated with the inorganic surface (Figure 6d) and the effect of Ca^{2+} on the rate of perylene adsorption is minimal relative to a NaCl solution (Figure 7). At pH 7 and 10, however, the binding of Ca^{2+} is appreciable at the silica surface; large differences in adsorption rates relative to those for NaCl solutions are also observed for samples with Ca^{2+} at these pH values.

Interestingly, while the binding of Na^+ to silica suppresses the initial rate of perylene adsorption, the presence of surface-bound Ca^{2+} appears to favor the rate of

adsorption. The reasons for these observations are not clear. It may be possible that the presence of Ca^{2+} near the surface somehow alters the structure of water (i.e., the organization of water molecules) in the interfacial region in a manner which makes the surface more receptive to hydrophobic molecules. While the presence of Na^{+} at the silica surface also influences the rate of perylene adsorption, the effect is opposite to that observed for Ca^{2+}.

For the few long-term adsorption studies performed, ionic strength effects analogous to those observed for the rate of adsorption were not seen. For example, although the rate of perylene adsorption at pH 4 varied with ionic strength (Figure 7), the extent of adsorption appeared to be insensitive to the background electrolyte (Table IV). Whether Ca^{2+} and Na^{+} would have affected the extent of perylene adsorption on the silica surface at higher pH values is unknown; long-term adsorption data were not available at higher pH values. More work needs to be done to determine if changes in aqueous chemistry affect the extent of adsorption of a HOC on inorganic surfaces.

The fact that an equation with two exponential terms was required to fit the kinetic adsorption and desorption data in the long-term adsorption studies is puzzling. There is precedence, however, in analyzing adsorption/desorption data in this manner. For example, Karickhoff (1980, 1984) proposed a two-stage kinetic model to describe the sorption of HOC by sediments. The model assumed that two types of surfaces existed with which HOC solute molecules could associate. Kinetic factoring was modeled by allowing one component to react rapidly (equilibration

within a few minutes) while the other reacted much slower (characteristic times ranging from minutes to weeks).

The model proposed by Karickhoff (1980, 1984) seems appropriate for use with natural sorbents (e.g., sediments and soils) in which two possible reservoirs for HOC can be readily identified: an organic compartment and an inorganic compartment. The fast step would therefore be characteristic of partitioning into organic material, while the slow step would be indicative of adsorption to mineral surfaces and, particularly, diffusion into constricted internal pores in the mineral matrix or between layers of expanding clay minerals.

In this study, no organic material was present in the system and a nonexpanding mineral with negligible surface porosity was the sorbent. It appears, therefore, that two processes may be operative in the adsorption of HOC to inorganic surfaces which have not been observed previously. Alternatively, it may be argued that more than two processes are occurring and that a two-exponential equation merely fits the observed data because of the relatively large number of fitting parameters. Attributing the observed data to the presence of different surface sites does not seem warranted, considering that adsorption of HOC on inorganic surfaces is postulated to be driven primarily by the hydrophobic effect.

The nature of the two processes which appear to be operative in the adsorption reaction is not clear; possible mechanisms include solute diffusion on the mineral surface, the displacement of water molecules at the mineral surface by adsorbing solute molecules, solute diffusion through water at the solid-liquid

interface, and/or the perturbation and restructuring of water molecules in the interfacial region during HOC adsorption.

The resolution of the long-term kinetic data into two characteristic parts was not observed for the short-term adsorption data. It may be that the lower rate of mixing utilized in the short-term studies enhanced the contribution of mass transfer to the overall rate of perylene adsorption and thereby obscured the presence of the two characteristic times for adsorption observed in more vigorously mixed samples.

Prior studies of nonpolar HOC adsorption on inorganic surfaces have conflicted on the role of the mineral surface in the adsorption process. For example, Schwarzenbach and Westall (1981) and Murphy et al. (1990) observed that the type of surface was important in the adsorption of HOC in their studies; however, Keoleian and Curl (1989) and Backhus (1990) both found that differences in HOC sorption among the sorbents they studied could be explained solely by differences in surface area. Data from these studies are shown in Figure 8 along with the equilibrium results obtained in this work. Data are shown only for nonpolar, nonionic HOC for the reasons discussed in the Introduction.

From Figure 8, it appears that both arguments on the role inorganic surfaces play in adsorption may be correct, depending on the scale of γ_i^w used to evaluate the data. In the studies of Schwarzenbach and Westall (1981) and Murphy et al. (1990), there were discrepancies among the values obtained when different sorbents were used. However, these studies were not performed over a wide range of γ_i^w. If the data in Figure 8 are examined on a small scale, differences in K_w^{eq} are observed for

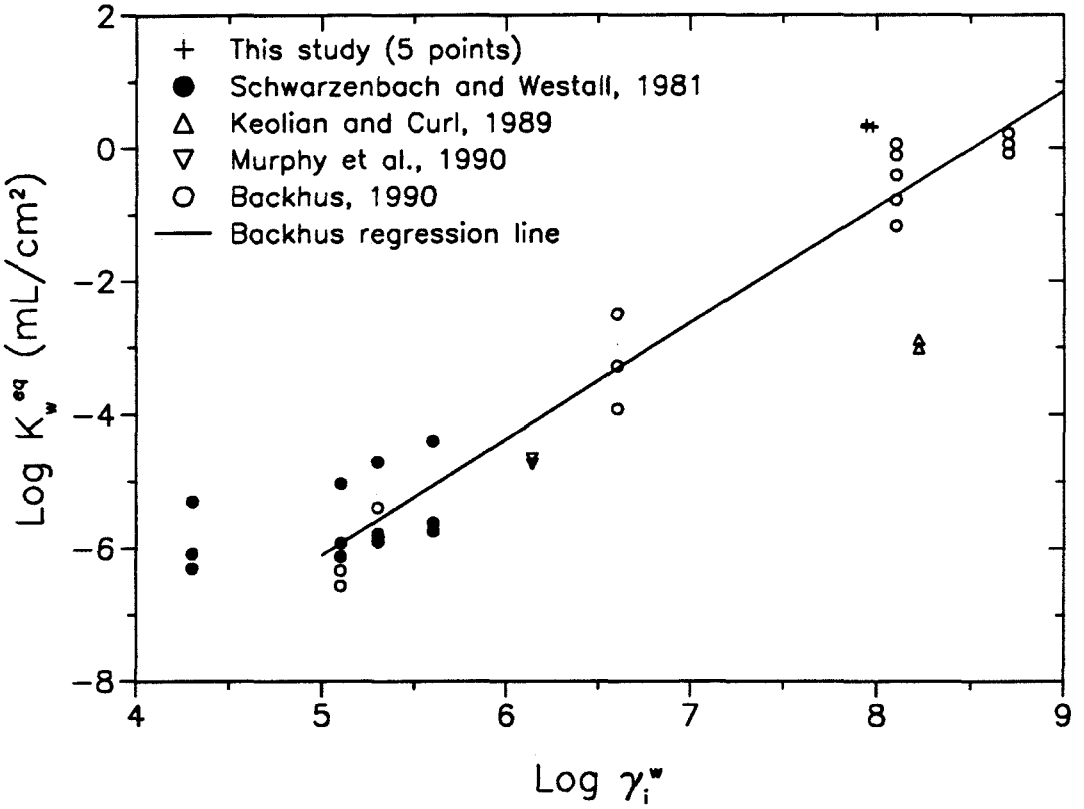

Figure 8. Adsorption of nonpolar HOC on various inorganic surfaces as observed by different researchers. Data are shown on a log-log plot of adsorption constants (normalized by surface area) versus aqueous activity coefficients. The line shown is the correlation obtained by Backhus (1990) upon regressing her data.

all of the studies which utilized different inorganic surfaces. If the data are examined over the entire range of solutes, however, a clear correlation exists when the adsorption constants are normalized by the surface area of the minerals. As discussed by Backhus (1990), the lower limit of this correlation appears to be $\gamma_i^w \sim 5$ because experimental artifacts become increasingly large for less hydrophobic solutes.

The normalization of adsorption constants by the surface area of the mineral in HOC-mineral systems is entirely analogous to the normalization of partition coefficients by the fraction of organic carbon in HOC-sediment systems. In the latter case, a first approximation reduces the dependence of partition coefficients to sorption on organic matter only. Therefore, unnormalized partition coefficients which tend to be variable over several orders of magnitude for a given solute with different solids can be reduced to normalized coefficients which generally vary only by factors of three to five for a given solute (Curtis et al., 1986a). As discussed by Karickhoff (1984), initial model development for describing adsorption reactions in complex systems depends on elucidating the essential phenomenological behavior while neglecting "second-order" effects. In this context, adsorption of a particular HOC to inorganic surfaces is observed to depend primarily on the surface area of the mineral. Variations in the extent of adsorption for different types of inorganic surfaces are then observed to be second-order effects.

Kinetics of Adsorption on Silica versus Natural Sorbents. The kinetic results observed above for the adsorption of perylene by fused silica contrast with those using natural materials with low f_{oc}. In this study, the adsorption reactions reached

equilibrium in approximately 2½ to 4 hours. These relatively short times agree qualitatively with the observations of Keoleian and Curl (1989) and Backhus (1990), who observed that adsorption equilibration was reached after two hours and ten hours, respectively.

The times required to reach sorption equilibrium in natural aquifer material, however, have been reported to be from days to years (Curtis et al., 1986b; Ball and Roberts, 1991a,b). The long equilibration times necessary for natural materials are thought to reflect an intraparticle process whereby a hydrophobic solute is slowly incorporated into either particle aggregates or sorbent components (Karickhoff, 1984). The incorporation into the sorbent matrix is postulated as being responsible for the relative resistance to extraction observed for some sorbed chemicals. This behavior is exemplified by the increasingly difficult recovery of sorbed compounds as the incubation time increases; observations of the phenomena have been described as an "aging" of the sorbed compound (Voice and Weber, 1983).

Ball and Roberts (1991a,b) found that the sorption of tetrachloroethene (PCE) and tetrachlorobenzene (TeCB) onto sandy aquifer material required contact times on the order of tens to hundreds of days to reach equilibrium and that physical adsorption to mineral surfaces appeared to be the most significant contribution to the total amount of PCE and TeCB sorbed. They also reported that although TeCB was sorbed ~40 times more strongly than PCE, the rate of sorptive uptake for TeCB was slower than that for PCE. This inverse relationship between the rate of adsorption and the strength of adsorption has been reported previously (Karickhoff, 1980, 1984).

The rate of sorptive uptake was modeled by Ball and Roberts (1991b) utilizing an intraparticle diffusion model which incorporated retarded transport in the constricted internal pores. The model, which predicts that the apparent pore diffusion rates will be inversely proportional to retardation, successfully described the relative rates of adsorption for PCE and TeCB. The interpretation of retarded diffusion in constricted pores concurred with the observation that extremely long extraction times (230 days) were required to recover the sorbed compounds from unaltered material, while a shorter time (30 days) was sufficient for extracting pulverized material.

The long extraction times required by Ball and Roberts (1991a,b) are similar to previously reported results for quantitative recovery of highly sorbed HOC solutes from natural materials (Karickhoff, 1984). These observations can be compared to the methanol extractions performed in this study. For the nonporous fused silica surface used here, quantitative recovery of the adsorbed perylene was accomplished in 5 to 10 minutes.

SUMMARY AND CONCLUSIONS

This study investigated the sorption of a fluorescent hydrophobic organic probe on an inorganic surface. The focus of the investigation was principally on the initial kinetics of the adsorption and desorption reactions between perylene and fused silica. Perylene, a nonpolar hydrophobic organic compound (HOC), was selected in order to eliminate or minimize possible sorption mechanisms other than hydrophobic interactions, while the interior walls of fluorescence cells were chosen as the model mineral surface in order to eliminate separation of the solid and aqueous phases. A principal hypothesis was that the rate and extent of adsorption would be dependent on the aqueous activity coefficient of perylene and the relative hydrophobicity of the silica surface. Because both of these parameters are affected by solution chemistry, a study of the influence of pH, ionic strength and background electrolyte composition on the rate and extent of adsorption was performed. A primary goal was to elucidate the role of a mineral surface in the adsorption process.

Fluorescence was utilized to monitor the loss of perylene from aqueous solution. The rate of perylene adsorption on silica was observed to increase with increased mixing. The effects of solution chemistry on the short-term adsorption of perylene were significant. At constant ionic strength the rate of adsorption decreased with increasing pH for all samples, both in the presence and absence of Ca^{2+}. In NaCl solutions, increases in the electrolyte concentration resulted in an increase, no change, and a decrease in adsorption rates for samples at pH 4, 7, and 10, respectively. The presence of Ca^{2+} had little effect on the rate of perylene adsorption

at pH 4 relative to NaCl solutions; however, at pH 7 and 10 the presence of Ca^{2+} greatly increased the adsorption rate relative to NaCl solutions of similar total ionic strength.

In contrast to the short-term adsorption results, there were no obvious trends with varying solution chemistry for the long-term adsorption studies and for the desorption studies. The time required to reach equilibrium in the long-term adsorption studies ranged from 2½ to 4 hours, while an apparent equilibrium was attained in 60 to 90 minutes for the desorption studies. Quantitative recovery of adsorbed perylene from the nonporous fused silica surface was observed after a 5- to 10-minute methanol extraction.

The aqueous activity coefficient of perylene and the surface speciation of silica were determined for the solution chemistry conditions examined in an attempt to correlate observed adsorption rates with solute and surface properties. Changes in the observed rate of adsorption at pH 4 appeared to depend solely on the fugacity of perylene, because little change in the surface speciation of silica occurred with varying salt composition at this pH value. At pH 7 and 10, however, the binding of cations at the inorganic surface becomes significant. In NaCl solutions at pH 7, little variation in the rate of adsorption was observed with increasing ionic strength because the increased binding of Na^+ at the silica surface apparently offset the increasing perylene fugacity. At pH 10, the decreasing surface affinity for perylene suppressed the solute's increasing fugacity and the rate of adsorption decreased with increasing NaCl concentration. Binding of Ca^{2+} at the silica surface had an effect on

the rate of perylene adsorption opposite to that of Na^+; at pH 7 and 10, the rate of adsorption increased in the presence of Ca^{2+} relative to NaCl solutions.

From the long-term adsorption data, it appears that two (or possibly more) different processes are operative in the adsorption of nonpolar HOC to bare mineral surfaces. The nature of these processes is not clear, but may relate to the structure of water in the solid-liquid interfacial region.

The role of a mineral surface in the adsorption of nonpolar HOC has been debated by previous researchers. It is proposed in this chapter that normalization of an adsorption constant by the area of a mineral surface is analogous to the normalization of a partition coefficient by the fraction of organic carbon in a sorbent. The adsorption of a particular HOC to inorganic surfaces would thus depend primarily on the surface area of the mineral, while variations in the extent of adsorption for different types of minerals will be second-order effects.

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Chapter 6

CONCLUSIONS

The objective of this research was to investigate sorption reactions of hydrophobic organic compounds (HOC) under laboratory conditions selected to model natural water systems. Polycyclic aromatic hydrocarbons (PAHs) were utilized as surrogates for HOC because (1) PAH compounds fluoresce in aqueous solution, thus very low solute concentrations can be measured by fluorescence techniques, (2) PAH compounds are nonpolar molecules and therefore all sorption interactions between the organic solutes and sorbents are primarily controlled by hydrophobic interactions, and (3) PAH compounds are among the most widespread of all hydrophobic organic pollutants and are known to be risks to human health.

Hydrophobic compounds, as their name implies, have relatively low solubilities in water and tend to adsorb at surfaces and, particularly, associate with natural organic material (NOM) in the environment. An understanding of adsorption mechanisms, therefore, is an important key to describing the fate of HOC in the environment because sorption reactions directly affect the mobility, chemical reactivity, bioavailability, and toxicity of hydrophobic compounds.

In Chapter 2, the binding of anthracene, pyrene and perylene by well-characterized humic substances was examined. A major goal was to elucidate the fundamental mechanisms by which these compounds associate with dissolved humic material. Two molecular-level models of HOC-NOM interactions were presented. The first model views the interaction as a dissolution of the solute into an organic-like phase present in NOM. The second model pictures the HOC-NOM association as a process which involves the solute fitting into voids or cavities which exist in the

NOM structure. Because these two models have different interaction schemes, their dependence on changes in aqueous chemistry will be different. By varying the pH, ionic strength and composition of the background electrolyte, the influence of solution chemistry on carbon-normalized partition coefficients should thus distinguish between the two models.

The binding of PAH solutes by dissolved humic material was observed to be complete always within 3 minutes and at times within 20 seconds. In general, increases in salt concentration decreased the binding of PAHs. This observation suggests that the humic material utilized in this study does not form "microscopic organic environments" into which HOC can dissolve. This conclusion is supported by the relatively low molecular weight of the humic substances. Instead, the picture of humic material as an open structure with hydrophobic cavities seems more plausible. Because the dimensions and hydrophobicity of the voids would be sensitive to variations in solution chemistry, a subsequent change in the ability to bind HOC would occur similarly to the trends observed in Chapter 2.

In Chapter 3, the adsorption of humic substances on colloidal-sized aluminum oxide particles was investigated in order to study the formation of organic coatings on mineral surfaces. It was postulated that the mechanisms by which humic material is adsorbed to minerals greatly influence the type of surface complex which is formed, and that different types of surface complexes bind pollutant molecules dissimilarly.

Adsorption densities for both humic and fulvic acid showed good agreement

with Langmuir isotherms, and qualitative interpretations of the adsorption processes were made utilizing parameters from the Langmuir model. Several differences in the adsorption of humic and fulvic acid were noted, and these differences appeared to result from the operation of different adsorption mechanisms. For fulvic acid, ligand exchange was the most important adsorption mechanism for all conditions examined. Although ligand exchange was also a major adsorption mechanism for humic acid, other mechanisms contributed to adsorption as the solution composition and humic acid concentration changed. The additional mechanisms were postulated to be hydrophobic bonding, Na^+ bridging and water bridging.

The results obtained in Chapter 3 were utilized in Chapter 4 where the binding of perylene by organically-coated particles was examined. The association of perylene with humic substances adsorbed on aluminum oxide particles versus the same humic material freely dissolved in aqueous solution was compared. It was postulated that the mechanisms by which humic substances are adsorbed to minerals greatly influence the ability of the adsorbed humic material to bind nonpolar HOC.

For all systems examined, adsorption of the humic substances on alumina decreased the ability of humic material to bind perylene. The effect of solution chemistry, apart from its influence on changing the characteristics of the dissolved material, was to alter the mechanisms of humic material adsorption on alumina. Different adsorption mechanisms will determine how tightly bound organic material is held at mineral surfaces. The ability of weakly-adsorbed humic acid to bind perylene, and possibly many of its other properties, approaches that of dissolved

humic material.

In the absence of sufficient amounts of organic carbon, adsorption of HOC to bare mineral surfaces may be an important reaction in natural waters. In Chapter 5, the adsorption of perylene on fused silica was examined. The focus of the investigation was principally on the initial rates of adsorption and desorption. A key hypothesis was that the rate and extent of adsorption should be dependent on the fugacity of perylene and the relative surface hydrophobicity of silica. Because both of these parameters are affected by solution chemistry, the influence of pH, ionic strength and background electrolyte composition on adsorption was examined.

Although the rate of perylene adsorption on silica appeared to correlate with increasing solute fugacity and increasing surface hydrophobicity in the short-term adsorption studies, no obvious trends with varying solution chemistry were observed in limited long-term adsorption and desorption studies. The time required to reach equilibrium in the long-term adsorption studies ranged from 2½ to 4 hours, while the desorption reaction was apparently equilibrated in 60 to 90 minutes. Quantitative recovery of adsorbed perylene from the nonporous fused silica surface was observed after a 5- to 10-minute methanol extraction. From the long-term data, it appeared that two different processes were operative in the adsorption of perylene on silica. The nature of these processes is not clear, but may relate to the structure of water at the solid-liquid interface.

A primary goal in Chapter 5 was to elucidate the role of mineral surfaces in the adsorption of nonpolar HOC. It was proposed in that chapter that normalization

of adsorption constants by mineral surface areas is analogous to the normalization of partition coefficients by the fraction of organic carbon in sorbents. Adsorption of a particular HOC thus depends primarily on the exposed surface of the mineral, while variations in the extent of adsorption for different types of minerals are second-order effects.

In many research projects the questions that are generated during an investigation appear to outnumber the answers that are being obtained (Could this be a cruel trick of the second law of thermodynamics?). This is particularly evident in thesis research, which often is conducted within limited time-frames and, more importantly, with limited knowledge at the start of the project (How many times can one researcher think to himself: "If only I had known this before!!!?"). True to form, the results presented in this thesis leave many questions unanswered. Several of these questions, and possible future research opportunities are:

(1) Will all interaction mechanisms between nonpolar hydrophobic pollutants and NOM be similar to that observed in this study? For example, the molecular-level interactions for electron-rich hydrophobic compounds (e.g., PAHs) and electron-deficient compounds (e.g., PCBs) with natural organic material may be drastically different. This problem needs to be addressed with additional investigations of varying classes of organic pollutants and with either well-characterized and/or fractionated humic material or model compounds which can act as surrogates for humic substances.

(2) Is the binding of HOC by NOM a reversible reaction? Although the sorption/partitioning of HOC with organic material is often studied, the corresponding desorption reactions are seldom investigated. The rate of release of hydrophobic pollutants from NOM needs to be studied in order to obtain a better understanding of the fate of pollutants.

(3) What are organic coatings? In the environment NOM adsorbs at particle surfaces and can dominate the properties of the solid-liquid interface. As was observed in Chapter 4, particle-contaminant interactions depend to a great degree on the physical and chemical characteristics of the organic "film" which is coating particles. It is necessary, therefore, to gain a better understanding of what these characteristics may be.

(4) What is water? The answer to this seemingly trivial question is of great importance if we are going to comprehend HOC-water interactions. A better understanding of the structure of water is needed, particularly the structure of coordination shells which solvate nonpolar molecules and the structure of water at solid-liquid interfaces. This information would provide insight to the observations of Chapter 5. For example, what are the two different processes that apparently are operative in the adsorption of perylene to silica? When adsorbed at a fused silica surface, why do Ca^{2+} and Na^{+} have opposite effects on the rate of perylene adsorption?

A better understanding of the four topics above would prove useful in better predictions of the fate of hydrophobic organic pollutants in the environment.